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Study of Removal Processes for Halogenated Air Pollutants

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16. ABSTRACT

The fate of halocarbons released into the atmosphere from anthropogenic sources and their potential impact on the stratospheric ozone layer has been studied. Experimental kinetic data have been obtained for the reaction of OH radicals with CH_3Cl, CH_2Cl_2, $CHCl_3$, C_2H_5Cl, $C_2H_4Cl_2$, CH_3CCl_3, C_2Cl_4, $C_2H_4Br_2$, and CO. Best values for the OH + halocarbon rate constants have been assessed and tropospheric lifetimes calculated.

The kinetics of the homogeneous gas phase hydrolysis of the secondary anthropogenic halocarbon pollutants, CCl_3COCl, CCl_2HCOCl, $CClH_2COCl$, and $COCl_2$ have been studied. The rate studies show that removal by gas phase hydrolysis would have halflives in excess of 100 years. Some preliminary heterogeneous rain out studies have been made on CCl_3COCl, which though not conclusive, suggest that rain out would probably be an effective sink for its removal but that the uncertainties are such that this mechanism requires further study.

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STUDY OF REMOVAL PROCESSES FOR HALOGENATED AIR POLLUTANTS

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ABSTRACT

This study is concerned with the fate of some chlorinated compounds, released into the atmosphere from anthropogenic sources, and their potential impact on the stratospheric ozone layer. The study may be divided conveniently into three parts:

(1) An investigation of hydroxyl radical reaction kinetics with CH_3Cl, CH_2Cl_2, $CHCl_3$, C_2H_5Cl, $C_2H_4Cl_2$, CH_3CCl_3, C_2Cl_4, $C_2H_4Br_2$ and CO, under conditions closely resembling those found in the atmosphere, using a competitive rate method. Best values for the OH + halocarbon rate constants have been assessed based on the presently derived data and that existing in the literature. Tropospheric lifetimes have been calculated, which, with the possible exception of CH_3CCl_3, indicate that none of these compounds will enter the stratosphere as such in significant amounts. CH_3CCl_3 does not at present represent a problem, but could, if anthropogenic releases kept increasing give reason for concern. The previously unsuspected pressure dependence of the OH + CO reaction in air-like mixtures has been established. This knowledge will be of great value in better understanding the chemistry of polluted atmospheres.

(2) An investigation of the homogeneous gas phase hydrolysis kinetics of the secondary anthropogenic halocarbon pollutants CCl_3COCl, CCl_2HCOCl, $CClH_2COCl$ and $COCl_2$. These data were obtained using a static reactor in the temperature range 470-620°K. The derived rate constants were used to determine tropospheric half lives for these species against hydrolysis. In all case values in excess of 100 yrs resulted indicating that in the absence of other removal mechanisms, large quantities of these materials would enter the stratosphere.

(3) An investigation of the heterogeneous "rain out" rate of the secondary anthropogenic halocarbon pollutants noted above. A simple model for the atmospheric "rain out" of these species was constructed based on gas collision kinetic theory. This model requires the determination of an effective rain drop-acid chloride sticking coefficient. Some preliminary experimental data were obtained for CCl_3COCl which indicated that "rain-out" would probably be an effective removal mechanism for this species from the atmosphere. However, the preliminary nature of the data, the surprisingly low value of the sticking coefficient obtained, and the admitted fact that insufficient experimentation was made to determine the true effective sticking coefficient for atmospheric application, strongly suggest that further studies should be made before firm conclusions can be obtained with respect to the effectiveness of "rain-out" as an atmospheric removal mechanism for these species.

Recommendations for future studies and the fate of these halocarbon acid chlorides are made.

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SECTION 1

INTRODUCTION

Interest in the fate of halogen compounds introduced into the atmosphere from anthropogenic and natural sources has been stimulated by their theorized potential threat to the stratospheric ozone layer.[1-5] Initially the major concern was directed at the "Freons," chlorofluoromethanes widely used as aerosol propellants and refrigerants. These compounds apparently have no atmospheric sink, they diffuse to the higher regions of the atmosphere (stratosphere) where they are dissociated by short wavelength radiation (190-220 nm) to yield atomic chlorine and fluorine. The major problem lies with the atomic chlorine which can take part in the catalytic decomposition of ozone, via the series of reactions:

$$Cl + O_3 \rightarrow ClO + O_2$$

$$O_3 + h\nu \rightarrow O_2 + O \qquad \text{Net } 2O_3 = 3O_2$$

$$ClO + O \rightarrow Cl + O_2$$

Although there are some sinks for the chlorine in the stratospheric (e.g., HCl) its removal in this form by normal diffusion process is slow. If there are large fluxes of chlorine bearing compounds to the stratosphere, there appears to be a real danger that their accumulation could result in a significant reduction in the earth's ozone layer. Eventual reduction of the ozone layer by some 10-15% has been postulated within 20-30 years if the scale of present emissions of Freons continue. The actual consequence of such an ozone reduction would be to increase the amount of UVB radiation (290-310 nm) the earth receives. The

precise result of this increased UV radiation on life is not clearly defined but increases in skin cancer, plant life damage and possible adverse chemical effects have been suggested.[6]

As noted above, the initial concern was with the Freons, however, it was shortly thereafter that the potential danger associated with anthropogenic releases of halocarbons into the atmosphere was also realized. In an Environmental Protection Agency study,[7] the size and nature of the anthropogenic emissions of halogen compounds was tabulated. A summary of these data is presented in Table 1. It was pointed out that the only known sink for most of these compounds in the troposphere is attack by OH radicals which exist in the atmosphere at a concentration of 2-6 x 10^5 molecules cm^{-3}.[8] If the reactions with OH are fast enough, then most of the compounds will be destroyed before they have chance to diffuse into the stratosphere and suffer photolysis with subsequent effect on the ozone layer.

Table 2 shows the state or knowledge at that time with respect to potential destruction of the halocarbons in the atmosphere and the expected degradation products.[7] Estimated half-lives for these compounds were based on the then known rate constants for the halocarbon + OH reactions or on estimated values. In general OH + unsaturated halocarbon reaction rates are sufficiently rapid (bimolecular rate constants usually $> 5 \times 10^{-12}$ cm^3 $molecules^{-1}$ sec^{-1}. A notable exception is CCl_2CCl_2 for which $K \lesssim 2 \times 10^{-13}$ cm^3 $molecule^{-1}$ sec^{-1}[10,11]) that tropospheric lifetimes are << 1 year. Rate constant data for the saturated halocarbons + OH reactions, were not, with the exceptions of the Freons, too well defined. Their estimated lifetimes in many cases lay in the 0.1-1 year region, and gave reason for concern since tropospheric lifetimes of $\lesssim$10 years could result in a possibly significant transport of the halocarbons into the stratosphere.

Table 1

ESTIMATED EMISSIONS OF HALOGENATED COMPOUNDS INTO THE ATMOSPHERE

Compound	World production in 1973, millions of pounds	Principal Uses (and percent of total production)	Estimated emissions into the atmosphere in 1973	
			World total, millions of pounds	U.S. total, percent
Fluorocarbon-11	670	Aerosol propellant (78%)	600	50
Fluorocarbon-12	980	Aerosol propellant (47%) Refrigerant (34%)	740	50
Fluorocarbon-22	270	Refrigerant (66%)	120	50
Fluorocarbon-113	110	Solvent (85%)	100	50
Fluorocarbon-114	100	Propellant (91%) Refrigerant (9%)	70	50
Carbon tetrachloride	2090	Production of fluorocarbons (88%)	88	50
Chloroform	496	Production of fluorocarbons (90%)	12	50
Ethyl chloride	1210	Produce tetraethyl lead (85%)	29	55
Ethylene dichloride	26,400	Produce vinyl chloride (78%)	1250	35
Methyl chloride	880	Produce silicones (43%) and tetramethyl lead (38%)	11	60
Methyl chloroform	900	Metal cleaning (70%) and degreasing	835	60
Methylene chloride	935	Paint remover (40%)	760	55
Perchloroethylene	1650	Dry cleaning (65%)	1370	45
Trichloroethylene	1540	Metal cleaning (86%)	1390	30
Vinyl chloride	15,600	Produce polyvinyl chloride (89%)	774	25

Table 2

ATMOSPHERIC CHEMISTRY SUMMARY

Compound name and formula	Worldwide release in 1973 of chlorine, 10^9 lbs	Estimated half-life, years	Type of Reaction	Tropospheric chlorinated reaction products (and approximate percent of chlorine)	Chlorine in product, 10^9 lbs
Perchloro-ethylene, C_2Cl_4	1.17	0.01	Photooxidation initiated at double bond	Trichloro acetyl chloride (80%) Phosgene (10%) Hydrogen chloride (10%)	0.93 0.12 0.12
Trichloro-ethylene, C_2HCl_3	1.12	0.001	Photooxidation initiated at double bond	Dichloro acetyl chloride (70%) Phosgene (12%) Formyl chloride (8%) Hydrogen chloride (10%)	0.79 0.13 0.09 0.11
Ethylene di-chloride $C_2H_4Cl_2$	0.90	0.3	Photooxidation initiated by OH abstracting H	Mono chloro acetyl chloride (100%)	0.90
Methyl chloro-form, CH_3CCl_3	0.74	1.1	Photooxidation initiated by OH abstracting H	Trichloro-acetaldehyde (100%)	0.74
Methylene chloride CH_2Cl_2	0.63	0.3	Photooxidation initiated by OH abstracting H	Phosgene (100%)	0.63
Vinyl chloride C_2H_3Cl	0.48	0.0001	Photooxidation initiated at double bond	Formyl chloride (50%) Hydrogen chloride (50%)	0.24 0.24
Fluorocarbon-11, CCl_3F	0.46	100	Stratospheric photo-dissociation	Fluorocarbon-11 (100%)	0.46

Table 2 (cont.)

Compound name and formula	Worldwide release in 1973 of chlorine, 10^9 lbs	Estimated half-life, years	Type of Reaction	Tropospheric chlorinated reaction products (and approximate percent of chlorine)	Chlorine in product, 10^9 lbs
Fluorocarbon-12, CCl_2F_2	0.44	100	Stratospheric photo-dissociation	Fluorocarbon-12 (100%)	0.46
Carbon tetrachloride, CCl_4	0.084	100	Stratospheric photo-dissociation	Carbon tetrachloride (100%)	0.084
Fluorocarbon-22, $CHClF_2$	0.050	0.3	Photooxidation initiated by OH abstracting H	Carbonyl fluoride & chlorine monoxide (100%)	0.050
Ethyl chloride, C_2H_5Cl	0.015	0.3	Photooxidation initiated by OH abstracting H	Formyl chloride (100%)	0.015
Chloroform, $CHCl_3$	0.011	0.2	Photooxidation initiated by OH abstracting H	Phosgene (67%) Chlorine monoxide (33%)	0.008 0.003
Methyl chloride, CH_3Cl	0.007	0.4	Photooxidation initiated by OH abstracting H	Formyl chloride (100%)	0.007

Another difficulty with the tropospheric lifetime estimation stems from the requirement that the average atmospheric OH radical concentration must be known, since τ_e (tropospheric lifetime due to OH radical attack) = $[K[OH]_{av}]^{-1}$ where k is the rate constant for the reaction, halocarbon + OH, and $[OH]_{av}$ is the average [OH] concentration. At the time the EPA report was compiled, $[OH]_{av} \simeq 2 \times 10^6$ molecules cm^{-3} was generally thought to be the correct order of magnitude. More recently this value has been lowered to $2\text{-}6 \times 10^5$ molecules cm^{-3}[8] which, of course, has the effect of increasing tropospheric halocarbon lifetimes over those previously estimated.

Although OH radicals are capable of reacting with halocarbons this does not automatically remove them from the troposphere. In Table 2, the resulting expected degradation products from OH attack are also tabulated. For the chlorine only containing compounds, the major products are the mono, di and trichloroacetyl chlorides, trichloroacetaldehyde, phosgene, formyl chloride and hydrogen chloride. In the troposphere, formyl chloride is almost certainly rapidly hydrolyzed to formic acid and HCl, and as such, are purged from the atmosphere by rain. The fate of the other degradation products in the atmosphere was not so certain. The mono, di and triacetylchlorides and phosgene were believed to hydrolyze to the corresponding chloroacetic acids and hydrochloric acid via homogeneous gas phase hydrolysis with atmospheric water vapor. The acids would then presumably be washed out of the atmosphere.

The purpose of the present investigation was to resolve some of the above noted uncertainties with respect to the fate of halogenated hydrocarbons in the troposphere. Specifically, the program had two tasks.

The first task was to determine rate constants for the reactions of OH radicals with the following saturated halocarbons; CH_3Cl (methyl chloride), CH_2Cl_2 (methylene chloride),

$CHCl_3$ (chloroform), CH_3CH_2Cl (ethyl chloride), CH_2ClCH_2Cl (ethylene dichloride) and CH_3CCl_3 (methyl chloroform). During the course of the program data appeared which suggested that rate data also be obtained for $CCl_2=CCl_2$ (perchloroethylene) and CH_2BrCH_2Br (ethylene dibromide), and also for the pressure dependence of the OH + CO reaction. From the derived rate data, tropospheric lifetimes were to be estimated and the possible implications with respect to the stratospheric ozone problem assessed.

The second task was to determine homogeneous gas phase hydrolysis rates for mono, di and trichloroacetyl chlorides and phosgene. Again, from the derived data, tropospheric lifetimes were to be estimated and the possible implications with respect to the stratospheric ozone problem assessed. During the course of the program, it became obvious that the heterogeneous rate of removal of these compounds should also be investigated and some preliminary data were obtained.

The remainder of this report describes the work performed, and conclusions derived. Recommendations for future studies to clarify still existing uncertainties have been made.

SECTION 2

CONCLUSIONS

The results of the experimental studies of the kinetics of the OH radical reaction with CH_3Cl, CH_2Cl_2, $CHCl_3$, C_2H_5Cl, CH_2ClCH_2Cl, and CH_3CCl_3 lead to the conclusion, that, with the exception of some possible reservations concerning future increases in CH_3CCl_3 production and release to the atmosphere, the halocarbons listed will not make any significant contribution to the chlorine burden in the stratosphere compared to that made by the Freons 11 and 12. However, this refers only to the parent halocarbon. As pointed out in the E.P.A. assessment of the overall halocarbon - stratospheric ozone problem,[11] it is also necessary to consider the degradation products of the halocarbons after attack by hydroxyl radicals and subsequent oxidation in the atmosphere.

The results obtained from the study of the CO + OH reaction in O_2 + N_2 mixtures further confirm the contention[12,13,14,15] that the CO + OH reaction is pressure dependent. In addition, they indicate that the change from the low to the high pressure limiting value occurs in the range $100 < P < 300$ torr. From the available data, a value of $k_1 = 2.69 \pm 0.40 \times 10^{-13}$ cm^3 molecule^{-1} sec^{-1} is suggested for the high pressure rate constant. The derived value of $k(OH + \text{iso } C_4H_{10}) = 1.59 \pm 0.18 \times 10^{-12}$ cm^3 molecule^{-1} sec^{-1} obtained in the present study is not in very good agreement with the two other reported literature values. The reasons for this are not clear and the absolute value of this rate constant at the present time must be considered not well defined.

From the results of the experimental studies of the homogeneous gas phase hydrolysis of $CClH_2COCl$, CCl_2HCOCl, CCl_3COCl, and $COCl_2$, the tropospheric and stratospheric lifetimes of those compounds were determined. Using the usual formula,[16] halflives of all four compounds were determined to be > 20 yrs in the troposphere, and > 10^9 yrs in the stratosphere. Although there is a considerable uncertainty in the calculated lifetimes, a result of having to extrapolate values for the rate constants to considerably lower temperatures than that at which they were determined, there is no doubt that the lifetimes of these species due to homogeneous gas phase hydrolysis in the troposphere are indeed substantial and that unless other mechanisms are available for their removal there is no question that these species will all find their way into the stratosphere in large amounts. Kinetic data were not obtained for CCl_2HCOCl due to experimental difficulties but it is reasonable to assume that this compound will probably have a lifetime in the same range as the mono and trichloroacetyl chlorides. There is also no question that in the stratosphere, homogeneous gas phase hydrolysis will not occur except on a time scale which is absurdly large.

The study of the heterogeneous hydrolysis or "rain out" of $CClH_2COCl$, CCl_2HCOCl, and CCl_3COCl were preliminary in nature, however, in view of the uncertainties, and the distinct possibility that "rain out" may not be a very efficient removal mechanism for these compounds from the atmosphere, it is concluded that until further experimentation is made to determine reliable values of sticking coefficients for all these compounds, it is not possible to reliably assess the potential impact of these compounds on the stratospheric ozone layer, other than to note it could be substantial, since these compounds are formed and are present in the atmosphere at considerably larger levels than the Freons 11 and 12.

SECTION 3

RECOMMENDATIONS

As a result of the present program it is not clear whether "rain out" is an efficient mechanism for the removal of the secondary halocarbon pollutants from the lower troposphere which would prevent these compounds reaching the stratosphere. The compounds, namely mono, di and trichloroacetyl chlorides, phosgene and trichloroacetaldehyde, have a flux into the atmosphere which has the potential of carrying up to 5 times as much chlorine into the stratosphere as the Freons 11 and 12.

Preliminary "rain out" experiments for these compounds in the laboratory have been made, but only for CCl_3COCl with any precision. Even here further experimentation is required to be certain that the derived sticking coefficients is applicable to the real atmospheric situation. The present data suggest the distinct possibility that "rain out" for these compounds may not be a very efficient removal mechanism Because of this possibility, further study of the "rain out" problem is required. The model used to date in these studies is quite simple and has the advantage that relatively few experimental parameters need to be investigated in order to derive a realistic value for the sticking coefficient to be applied to the atmospheric situation. Once realistic tropospheric sticking coefficients have been obtained the efficiency of the "rain out" process for these compounds can be easily calculated, and their potential threat to the stratospheric ozone assessed. Should the "rain out" process be found to be inefficient, then a study of ice particle-

acid chloride interactions should also be investigated to determine their potential as atmospheric scavengers.

A further advantage of such a study would be the insight it would provide into the whole question of the efficiency of atmospheric "rain out" with respect to the removal of atmospheric trace gases. This aspect of the study would be particularly valuable since at the present time more and more concern is being directed at the fate of potential toxic substances in the environment. Finally, it would also be highly desirable to make tropospheric mixing ratio determinations for these species since, as of now, only limited data have been obtained for phosgene[17] and none are available for any of the other compounds.

Should the above study demonstrate that "rain out" is not efficient removal process for some, or all of these compounds, then alternative mechanisms for their removal should be investigated. One obvious possibility might be OH radical attack on the hydrogen containing compounds.

Finally, the results of the present study showing the pressure dependence of the OH + CO reaction in the atmosphere also raises another problem. The temperature dependence of the OH + CO reaction in it low pressure limit is known to be zero, but it is not known if it is zero in the high pressure regime. The latter would be of importance in the lower atmosphere with respect to its effect on the OH radical concentration and to enable better mathematical modeling predictions to be made. The temperature dependence of the OH + CO reaction should be determined in its high pressure region.

700 torr[15] and 100 torr.[15] At 100 torr, k was determined as 1.4×10^{-13} cm^3 $molecule^{-1}$ sec^{-1}, in good agreement with the accepted value of 1.5×10^{-13} cm^3 $molecule^{-1}$ sec^{-1}. At the higher pressures, values of 3.0×10^{-13}[15] and 2.7×10^{-13}[13] cm^3 $molecule^{-1}$ sec^{-1} were reported. Similar pressure dependent results were found by Heicklen[14] using H_2 and SF_6 as the make up gas. Additionally, it was shown that He as a third body, was much less effective in enhancing the reaction rate than H_2 or SF_6.

In our investigation of the OH + halocarbons reaction rates using the OH + CO as a competitive reference reaction, a total system pressure of 400 torr was used, with mixtures of oxygen and nitrogen, similar to air, being used as the make up gas. In light of the above findings concerning the pressure dependence of the CO + OH reaction, and in view of the reaction's importance in atmospheric chemistry (the major sink for CO and halocarbons in the atmosphere is believed to be the hydroxyl radical) it was considered worthwhile to investigate the pressure dependence of the reaction in the 100-600 torr range using a make up gas consisting of oxygen and nitrogen in ratios similar to that found in air. Photolysis of hydrogen peroxide was the source of hydroxyl radicals, and competitive rate of attack of these radicals on CO and isobutane (the latter serving as the reference reaction) was used to deduce the OH + CO rate constant.

EXPERIMENTAL

The hydroxyl radical reactions were carried out in a static cylindrical quartz reactor (Figure 1) of about 1 liter capacity (25 cm long x 8 cm, dia.). The reactor was jacketed with a second quartz vessel equipped with input and output lines for a thermostated water supply to provide temperature control. Temperature stability was good to $\pm 0.2^{\circ}C$ with the reactor being held at $31.5^{\circ}C$ during the experiments. Three all teflon and

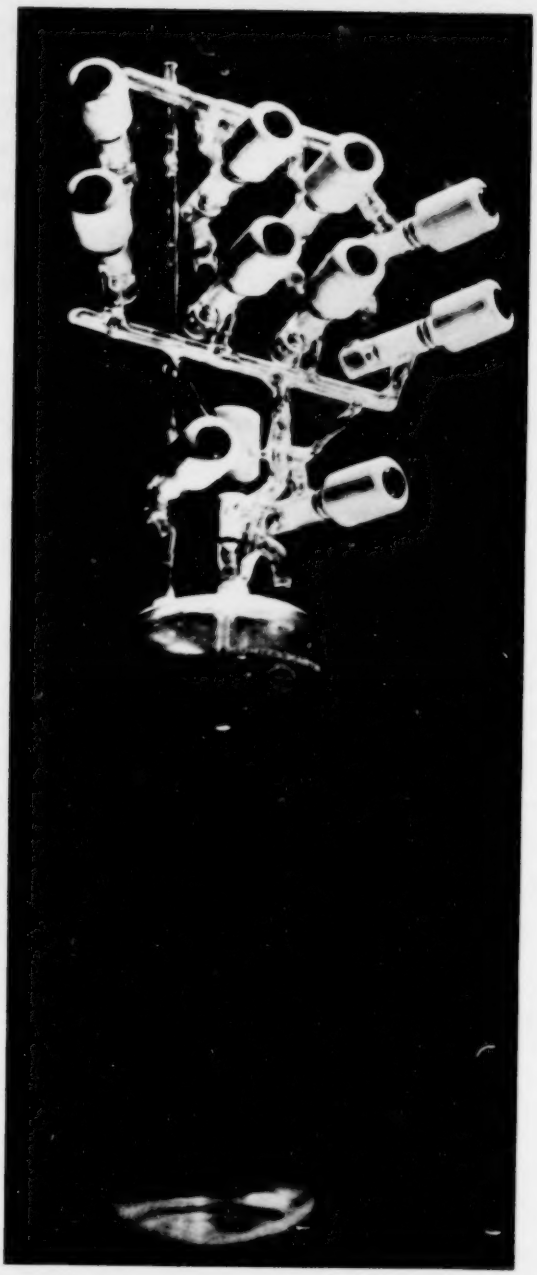

Figure 1. Static Photochemical Reactor, Showing Inlet and Outlet Ports and Gas Sampling Storage Volumes

glass valves were connected to the top of the reactor. Two of these were used for filling the reactor with H_2O_2 vapor and premixed reaction gases. The third, connected to a capillary tube projecting about 8 cm into the reactor was connected to four storage volumes of about 3 cm^3 each. The latter could be evacuated and filled with gas samples from the reactor for subsequent analysis.

The entire reactor assembly sat in the center of a Rayonet Model RPR-1000 Photochemical Reactor. Irradiation was provided by 15 RPR lamps with maximum intensity centered at 3000Å.

The reactor was connected to a mercury free vacuum and gas handling line which is shown in Figure 2 along with the rest of the experimental apparatus. Pumping was provided by a mechanical oil pump and a Varian ion pump. Pressures in the 10^{-7} torr range were routinely attained. The line was constructed of stainless steel tubing with the exception of the section used for handling the H_2O_2. This section was constructed of glass, with all glass and teflon valves. Three large volume vessels were used for mixing and storing reaction gases. A Wallace and Tiernan absolute pressure gauge calibrated against the vapor pressure of several liquids was used to measure pressures when making up reaction gas mixtures. Hydrogen peroxide pressures were measured with a silicone oil manometer. The latter was calibrated against a Barytron gauge, and also compared with oil density measurements.

Connected to both vacuum line and reactor via a gas sampling loop was a Varian Model 2700 Trace Gas Analyzer for the analysis of carbon dioxide samples from the reactor. The sampling loop had a volume of 8.9 cm^3. It could be opened to the vacuum line, the reactor gas storage volumes or isolated for injection into the chromatograph. Prior to filling, the sample loop was first evacuated and then opened to the gas

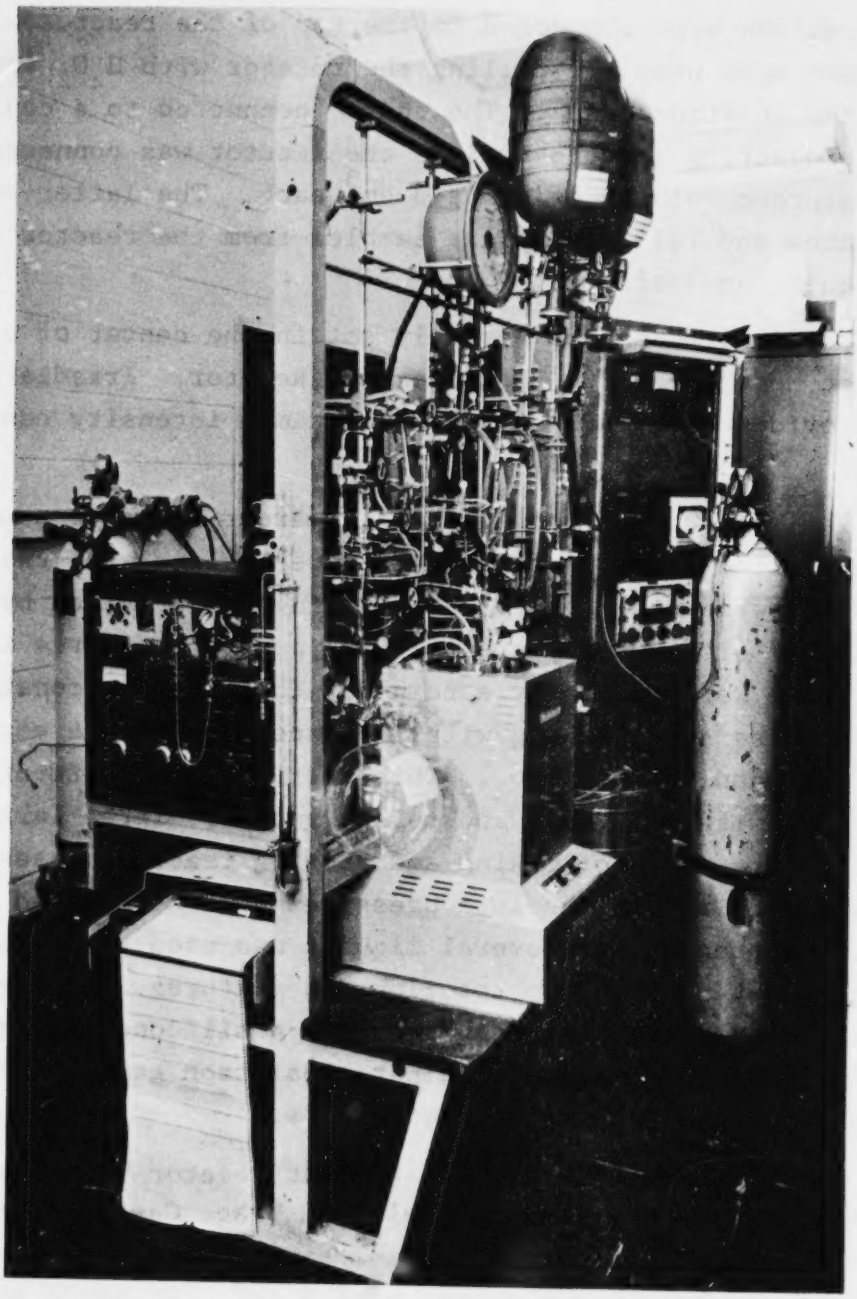

Figure 2. The Static Photochemical Reactor System, Showing, The Photochemical Reactor, Gas Chromatograph, Gas Storage Bottles and Vacuum Line

source of interest. Injection was accomplished via two three-way ball valves which allowed the carrier gas to flush the sample into the chromatograph. For CO_2 analysis, the chromatograph was fitted with a 10' x 1/8" stainless steel column packed with 80/100 mesh Poropak Q. Carrier gas flow (Matheson U.H.P. Helium) was set at 45 cm^3 min^{-1}, with the analysis run isothermally at 50°C. This resulted in a CO_2 retention time of about 2 minutes. The helium-ionization detector used on the trace gas analyzer has great sensitivity ($\sim 10^{-11}$ moles of CO_2 could be detected in an air sample). However, the detector response was non-linear and sensitive to column pretreatment. Accordingly, just prior to each experiment, the instrument was calibrated (Matheson Calibration gas, 498 ppm (v) CO_2 in air) in the range expected in the kinetic experiment (10^{-10} to 10^{-9} mole CO_2).

Gas mixtures of O_2, N_2, CO, and O_2, N_2, CO and isobutane were prepared using standard vacuum line P.V.T. techniques. Linde Zero Grade oxygen and nitrogen were used without further treatment. Carbon monoxide, Matheson research grade purity (min. 99.99%), was passed through a liquid nitrogen cold trap prior to use to remove possible metal carbonyls. Isobutane, 99% mole minimum purity from Phillips Petroleum Company, was used without further treatment.

90% H_2O_2 from F.M.C. was used in the experiments. It was analyzed by titration with a standard solution of $KMnO_4$. A degassed sample was stored in the vacuum line at liquid N_2 temperatures prior to use. All parts of the apparatus exposed to hydrogen peroxide were passivated using standard procedures[19] with a 25% solution of sulfuric acid. Prior to each experiment hydrogen peroxide vapor at a pressure of about 1 torr was left in the reactor for conditioning purposes. It was then evacuated in preparation for the experiment.

H_2O_2 vapor was the first component introduced into the reactor. The vapor was obtained from a thermostated H_2O_2 liquid sample maintained at a preselected temperature between 21°C and 24°C. The reactor was exposed to this vapor for two minutes and the pressure recorded. From the latter, the amount of H_2O_2 and H_2O vapor in the reactor was calculated.[19] Following this, the other gaseous components (which had been premixed and stored) were added until the desired reactor total pressure was attained. Approximately 18 minutes after initial H_2O_2 introduction, two gas samples were extracted from the reactor and analyzed for CO_2 (present as a minor trace impurity in the oxygen and nitrogen). Thirty minutes after initial H_2O_2 introduction, irradiation was initiated. The first four gas samples for analysis were extracted during the first 2-1/2 minutes of the experiment and retained in the storage volumes above the reactor. These four samples were then analyzed, and as an empty sample volume became available, a new sample was taken. A total of eight gas samples were extracted from the reactor in a time period of from 10-12 minutes.

RESULTS

The basic equation used to calculate the rate constant k_1 for the reaction $CO + OH \rightarrow CO_2 + H$ was as follows:[18,20]

$$k_1 = \frac{[isoC_4H_{10}]}{CO} \left[k_2 \left[\frac{L}{M} - 1 \right]^{-1} - \frac{k_3[H_2O_2]}{[isoC_4H_{10}]} \right]$$

where,

L = Initial rate of CO_2 formation with CO present in the reaction mixture and isobutane absent

M = Initial rate of CO_2 formation with both CO and isobutane present in the reaction mixture.

k_2 and k_3 are the rate constants for the hydroxyl radical reaction with isobutane and hydrogen peroxide respectively.

The reaction conditions under which this equation applies with respect to relative concentrations of the various reactants, H_2O_2:O_2 and H_2O_2:CO, have been defined in earlier studies[18,20] and were satisfied in the present investigation. From the experimental data, CO_2 production versus time was plotted graphically using a computer best fit for the data points. In all experiments the CO_2 production rates were almost, but not quite linear, showing a slight fall off with time as the experiment progressed. In order to take this slight curvature into account, the data were "best fitted" using a 2nd degree polynomial and the initial rate determined from the resulting regression equation.

In order to derive values for k_1 as a function of pressure, it was necessary to assign values to k_2 and k_3.

k_3, the rate constant for the H_2O_2 + OH reaction, has been the subject of two reviews[21,22] and three fairly recent determinations.[18,20,23] The latter gave $k_3 = 1.2 \pm 0.3 \times 10^{-12}$, $6.0 \pm 0.4 \times 10^{-13}$ and $8.4 \pm 1.7 \times 10^{-13}$ cm^3 $molecule^{-1}$ sec^{-1} and present little reason to change the earlier recommended value, $k_3 = 8.0 \pm 4.0 \times 10^{-13}$ cm^3 $molecule^{-1}$ sec^{-1}.[22] Two values are available for k_2, the rate constant of the OH + iso C_4H_{10} reaction. A flash photolysis study by Greiner gave $k_3 = 2.3 \pm 0.2 \times 10^{-12}$ cm^3 $molecule^{-1}$ sec^{-1}[24] and a competitive method using CO + OH ($k_1 = 1.5 \times 10^{-13}$ cm^3 $molecule^{-1}$ sec^{-1}) as a reference reaction yielded $k_2 = 3.5 \pm 0.8 \times 10^{-12}$ cm^3 $molecule^{-1}$ sec^{-1}.[18] These two values do not quite agree within the stated experimental errors, the reasons for this not being obvious. Because of the uncertainty in k_2, it was felt preferable to determine this quantity using CO + OH as the reference reaction at a total pressure of 100 torr. At this pressure, the CO + OH rate constant has its "low pressure value" of 1.50 x

In Table 3 the data used to evaluate k_2 are presented. A value of $1.59 \pm 0.18 \times 10^{-12}$ cm^3 $molecule^{-1}$ sec^{-1} was obtained, where the error limits represents the standard deviation of the experimental data points. This value is lower than either of the two previously determined rate constants for the reaction. The lack of agreement is most severe with respect to Gorse and Volman's determination, which was made using essentially the same technique. The discrepancy is difficult to account for, but could be due to an impurity in the isobutane sample. In Greiner's determination, a correction was made to the experimentally determined value of k_2 to take into account the destruction of OH by isobutyl radicals. This correction, amounting to approximately -10% of the experimental value, was based on an assumed value for $k(OH + C_4H_9)$ of 1.7×10^{-10} cm^3 $molecule^{-1}$ sec^{-1} and an assumed concentration of OH radicals of 5×10^{-11} molecule cm^{-3}. The lower value of k_2 determined here might indicate that Greiner underestimated the correction factor due to the $OH + C_4H_9$ reaction.

With the above determined value of k_2, the rate constants for the CO + OH reaction were determined as a function of total system pressure from the data presented in Table 3. Again, the quoted errors represents the standard deviation of the experimental data points. In Figure 3, the data are presented graphically, and for comparison the values obtained by Cox[13] and Calvert[15] in oxygen - nitrogen mixtures are also shown. The error limits associated with our data are relatively large 10-15% but unfortunately this is an inherent difficulty with the method. These data strongly suggest that the high pressure limit of the rate constant is achieved at 300 torr, and that the change from the low to the high pressure value occurs within the 100-300 torr pressure range.

Table 3

SUMMARY OF THE EXPERIMENTAL DATA FOR THE REACTION OH + CO

100 TORR TOTAL PRESSURE

Average System Composition (Torr)

	H_2O_2	H_2O	CO	iso-C_4H_{10}	O_2	N_2
without iso-C_4H_{10}	1.01	1.65	14.6	0.00	32.8	49.9
with iso-C_4H_{10}	1.06	1.73	14.6	1.24	32.8	48.6

Initial CO_2 Production Rates (mole-liter^{-1}-sec^{-1} x 10^9)

without iso-C_4H_{10} (3 expts): 8.18, 7,89, 7.91

with iso-C_4H_{10} (3 expts): 4.79, 5.09, 4.64

$K_1 = 1.50 \pm 0.24 \times 10^{-13}$ cm.^{3}-molecule^{-1}-sec.$^{-1}$

200 TORR TOTAL PRESSURE

Average System Composition (Torr)

	H_2O_2	H_2O	CO	iso-C_4H_{10}	O_2	N_2
without iso-C_4H_{10}	1.05	1.71	29.6	0.00	66.6	101.0
with iso-C_4H_{10}	1.06	1.73	29.6	2.51	66.6	98.5

Initial CO_2 Product Rates (mole-liter^{-1}-sec.$^{-1}$ x 10^9)

without iso-C_4H_{10} (4 expts): 9.04, 9.35, 8.95, 9.29

with iso-C_4H_{10} (4 expts): 5.32, 5.48, 5.17, 5.57

$K_1 = 1.65 \pm 0.16 \times 10^{-13}$ cm.^{3}-molecule^{-1}-sec.$^{-1}$

Table 3 (cont.)

300 TORR TOTAL PRESSURE

Average System Composition (Torr)

	H_2O_2	H_2O	CO	iso-C_4H_{10}	O_2	N_2
without iso-C_4H_{10}	1.31	2.12	23.0	0.00	51.8	221.7
with iso-C_4H_{10}	1.34	2.17	23.0	3.78	51.8	217.9

Initial CO_2 Production Rates (mole-liter^{-1}-sec.$^{-1}$ x 10^9)

without iso-C_4H_{10} (3 expts): 10.46, 10.82, 10.56

with iso-C_4H_{10} (4 expts): 5.93, 5.38, 6.05, 5.74

$K_1 = 2.66 \pm 0.32 \times 10^{-13}$ cm.^{3}-molecule^{-1}-sec.$^{-1}$

400 TORR TOTAL PRESSURE

Average System Composition (Torr)

	H_2O_2	H_2O	CO	iso-C_4H_{10}	O_2	N_2
without iso-C_4H_{10}	1.13	1.84	59.6	0.00	134.0	203.4
with iso-C_4H_{10}	1.15	1.87	59.6	5.06	134.0	198.3

Initial CO_2 Production Rates (mole-liter^{-1}-sec.$^{-1}$ x 10^9)

without iso-C_4H_{10} (4 expts): 10.90, 10.95, 10.08, 10.21

with iso-C_4H_{10} (4 expts): 7.33, 7.06, 6.34, 6.67

$K_1 = 2.35 \pm 0.45 \times 10^{-13}$ cm.^{3}-molecule^{-1}-sec.$^{-1}$

Table 3 (cont.)

500 TORR TOTAL PRESSURE

Average System Composition (Torr)

	H_2O_2	H_2O	CO	iso-C_4H_{10}	O_2	N_2
without iso-C_4H_{10}	1.21	1.94	38.6	0.00	86.8	371.5
with iso-C_4H_{10}	1.23	1.97	38.6	6.33	86.8	365.1

Initial CO_2 Production Rates (mole-liter^{-1}-sec.$^{-1}$ x 10^9)

without iso-C_4H_{10} (4 expts): 10.08, 10.05, 10.14, 10.23

with iso-C_4H_{10} (4 expts): 4.93, 5.59, 4.90, 5.55

$K_1 = 2.54 \pm 0.38 \times 10^{-13}$ cm.^{3}-molecule^{-1}-sec.$^{-1}$

600 TORR TOTAL PRESSURE

Average System Composition (Torr)

	H_2O_2	H_2O	CO	iso-C_4H_{10}	O_2	N_2
without iso-C_4H_{10}	1.19	1.93	46.4	0.00	104.3	446.2
with iso-C_4H_{10}	1.16	1.88	46.4	7.60	104.3	438.7

Initial CO_2 Production Rates (mole-liter^{-1}-sec.$^{-1}$ x 10^9)

without iso-C_4H_{10} (3 expts): 10.40, 9.94, 9.62

with iso-C_4H_{10} (3 expts): 5.73, 5.28, 5.35

$K_1 = 2.93 \pm 0.36 \times 10^{-13}$ cm.^{3} molecule^{-1}-sec.$^{-1}$

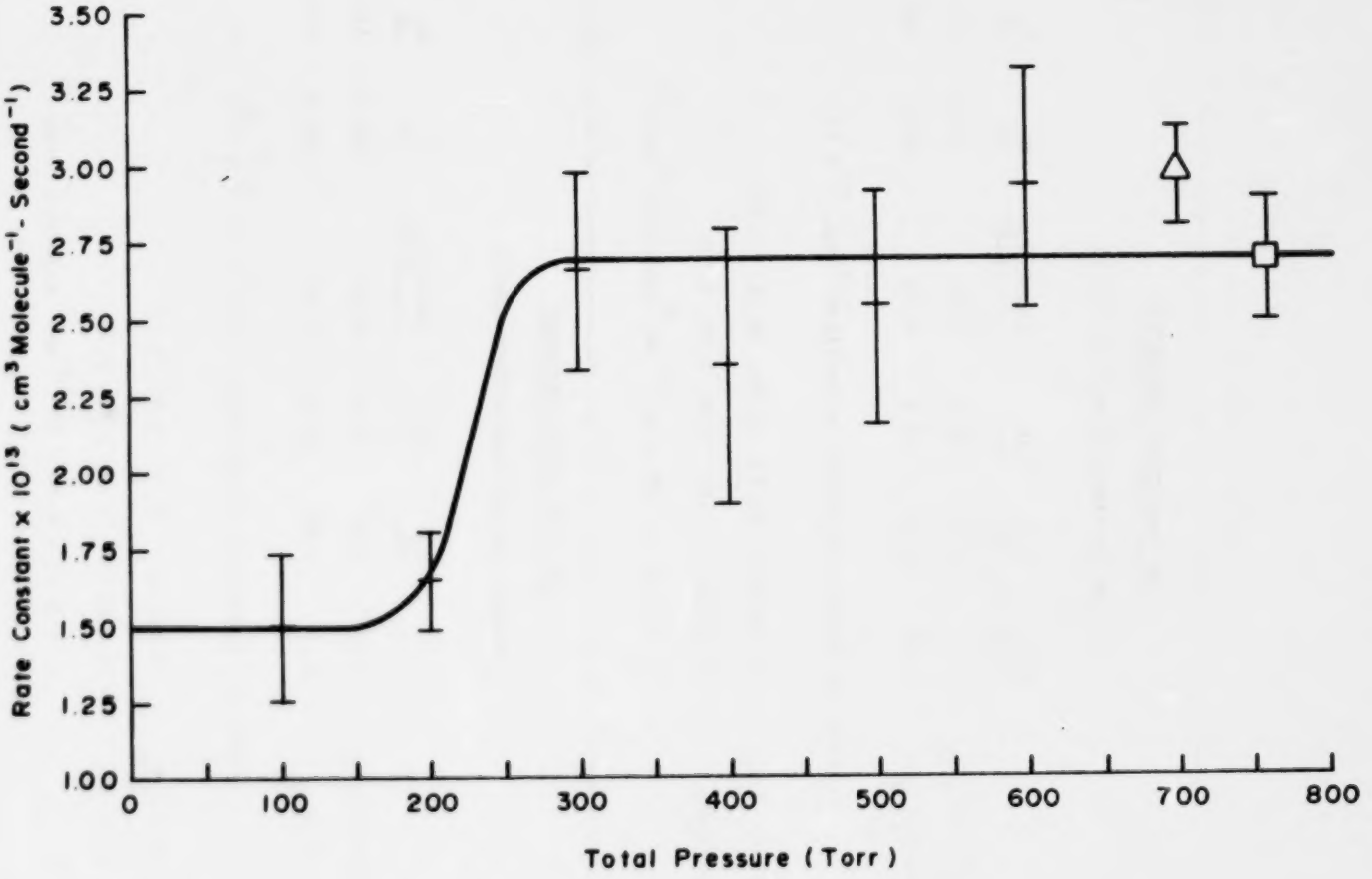

Figure 3. Pressure Dependence of the Rate Constant for the Reaction CO + OH → H + Present Data, ΔCox Etal[3] and □ Calvert Etal[4]

Taking a simple average of all the "high pressure" values ($P \geq 300$ torr) given in Figure 3, $k_1 = 2.69 \pm 0.23 \times 10^{-13}$ cm^3 molecule^{-1} sec^{-1}. Heicklen's high pressure data for k_1 were not included in Figure 3 since they were obtained in a hydrogen atmosphere, which apparently has an even greater effect on the reaction rate.[20] Both the Cox and Calvert high pressure values for k_1 are in substantial agreement with ours, though the value given by Calvert would be lowered from 2.97 to 2.07 x 10^{-13} cm^3 molecule^{-1} sec^{-1} if our value of $k_2 = 1.59 \times 10^{-12}$ cm^3 molecule^{-1} sec^{-1} had been used instead of Greiner's in their calculation of k_1.

Further support for the proposed high pressure value of $k_1 = 2.69 \pm 0.23 \times 10^{-13}$ cm^3 molecule^{-1} sec^{-1} comes from a determination in this laboratory of the rate constant for the OH + CH_3Cl reaction using the CO + OH reaction as the reference reaction (see Section 5 of this report). In an oxygen-nitrogen mixture at 400 torr, k(OH + CH_3Cl) was determined at $3.1 \pm 0.7 \times 10^{-14}$ cm^3 molecule^{-1} sec^{-1} with $k_1 = 2.69 \times 10^{-13}$ cm^3 molecule^{-1} sec^{-1}. The former value compares well with reported literature values of 3.6,[10] 4.2,[25] 4.6[26] and 5.95[12] x 10^{-14} cm^3 molecule^{-1} sec^{-1} determined using different methods.

SECTION 5

RATE CONSTANTS FOR THE REACTIONS OF OH WITH CH_3Cl, CH_2Cl_2, C_2H_5Cl, $ClCH_2CH_2Cl$, CH_3CCl_3, $C_2H_4Br_2$, $CHCl_3$ and C_2Cl_4 IN THE PRESENCE OF $O_2 + N_2$

KINETIC RESULTS USING THE STATIC REACTOR

Introduction

The possibility that anthropogenic releases of halogenated hydrocarbons can find their way into the stratosphere and be involved in a catalytic ozone destruction cycle has been well publicized.[2,27] In the troposphere these compounds are susceptible to attack by OH radicals, and this mode of reaction could act as a natural sink for these species, preventing them from diffusing into the stratosphere. In order to determine the likely efficiency of such a sink it is necessary to have kinetic data for the halocarbon-hydroxyl radical reaction rate. To date several groups of workers have been studying these reactions,[9,10,25,28,29,30,31] but with one exception,[29] all were made in the presence of inert gases, rather than oxygen and nitrogen mixtures as occurs in the atmosphere. Although it is not likely that these reactions are sensitive to the presence of different "third bodies," greater confidence could be placed in the rate date when applied to atmospheric chemistry, if the "third body" independence were established. For this reason, the present study was initiated. A competitive rate method was chosen in which the halocarbon competes with CO for available OH radicals.[2] The rate of formation of CO_2 in presence of halocarbon can then be related to the rate of OH attack on the halocarbon.

Experimental

The details of the experimental equipment and techniques have been described previously in Section 4 of this report. For this reason, only those details peculiar to the present study will be presented. Photolysis of H_2O_2 ($\simeq$90%) obtained from F.M.C. was used as the OH radical source, as in the previous study. The halocarbons, CH_3Cl and C_2H_5Cl from Matheson, were used without further purification except for vacuum line degassing. Chromatographic analyses indicated purities of >99.99 and 99%, respectively. CH_3CCl_3, CH_2ClCH_2Cl, and $C_2H_4Br_2$ (Eastman Kodak), CH_2Cl_2 and $CHCl_3$ (Fisher), and C_2Cl_4 (Baker) were all treated chemically to remove any unsaturated impurities. This, as experiments indicated here and elsewhere[9,10] was particularly necessary for CH_3CCl_3. Purification was accomplished as follows; Bromine, 1-2%, was added to the halocarbon and the mixture allowed to stand overnight. A solution of sodium thiosulfate was used to remove the bromine. This was followed by washing with water, a solution of sodium bicarbonate and finally water again. The halocarbon was dried over calcium chloride, carefully distilled and stored in light resistant bottles. Gas chromatographic analysis indicated the following purities; CH_3CCl_3 $\simeq$99.4%, $C_2H_2Cl_2$ $\simeq$99.9%, CH_2Cl_2 $\simeq$99.5%, $C_2H_4Br_2$ $\simeq$99.5%, $CHCl_3$ $\simeq$99.9% and C_2Cl_4 $\simeq$99.0%. Where possible, the amount of halocarbon added to the reactor was optimized to give the best precision in determining the rate constant. However, for CH_3CCl_3 and $C_2H_4Br_2$ the vapor pressures of the compounds were insufficient to enable the best conditions to be realized.

Gas mixtures of O_2, N_2, CO, H_2O_2 and halocarbons were prepared using standard vacuum line techniques as described previously in Section 4 of this report. Linde Zero Grade O_2 and N_2 were used without further treatment. Carbon monoxide, Matheson research grade purity (min 99.99%) was passed through

a liquid nitrogen cold trap to remove impurities prior to use. In all cases the total pressure in the reactor was adjusted to 400 mm Hg and the reaction run at 29.5°C. Photolysis of the hydrogen peroxide was made in a Rayonet Model RPR-1000 Photochemical Reactor using lamps with maximum intensity centered at 3000Å. Chromatography was used to monitor CO_2 production.

Results and Discussion

Under the conditions used in this study the following reactions were considered as important in interpreting the system's kinetics;[18]

$H_2O_2 + h\nu$	=	$2OH$	$2k_1 I_a$
$OH + H_2O_2$	=	$H_2O + HO_2$	k_2
$HO_2 + HO_2$	=	$H_2O_2 + H_2O$	k_3
$OH + CO$	=	$CO_2 + H$	k_4
$OH + RX$	=	$RX^{\cdot} + H_2O$	k_5
$H + O_2 + M$	=	$HO_2 + M$	k_7
$RX^{\cdot} + O_2$	=	$nCO_2 + ?$	k_8

$RX^{\cdot}$ is the radical formed due to hydrogen abstraction by OH on RX. With the exception of k_8, the reaction sequence is identical to that used by Volman. In the present study it was necessary to include k_8 since sometimes the experimental data clearly indicated that the halocarbon radical was also producing CO_2 in the system.

The above sequence of reactions may be treated in the usual way and the following sets of equations derived:

Case I with CO but no RX--

$$\frac{d[CO_2]}{dt} = L = k_4[OH][CO]$$

At steady state--

$$\frac{d[OH]}{dt} = 2k_1 \, Ia \, [H_2O_2] - k_2[OH][H_2O_2] - k_4[OH][CO] = 0$$

$$\therefore \quad \overset{\cdot}{OH}_{ss} = \frac{2k_1 I_a [H_2O_2]}{k_2[H_2O_2] + k_4 [CO]}$$

$$\therefore \quad \overset{\cdot}{L} = \frac{2k_1 I_a [H_2O_2] \, k_4[CO]}{k_2[H_2O_2] + K_4[CO]}$$

Case II with CO + RX and $k_8 = 0$--

$$\frac{d[CO_2]}{dt} = M = k_4[OH][CO]$$

At steady state--

$$\frac{d[OH]}{dt} = 2k_1 I_a [H_2O_2] - k_2[OH][H_2O_2] - k_4 [OH][CO] -$$

$$k_5[OH][RX] = 0$$

$$\therefore \quad \overset{\cdot}{[OH]}_{ss} = \frac{2k_1 \, I_a \, [H_2O_2]}{k_2[H_2O_2] + k_4[CO] + k_5[RX]}$$

$$\therefore \quad \overset{\cdot}{M} = \frac{2k_1 I_a [H_2O_2] k_4[CO]}{k_2[H_2O_2] + k_4[CO] + k_5[RX]}$$

Case III with CO + RX and $k_8 \neq 0$--

$$\frac{d[CO_2]}{dt} = M = k_4[OH][CO] + nk_8[RX\cdot][O_2]$$

At steady state--

$$\frac{d[OH]}{dt} = 2k_1 I_a[H_2O_2] - k_2[OH][H_2O_2] - k_4[OH][CO] - k_5[OH][RX] = 0$$

$$[OH]_{ss} = \frac{2k_1 I_a[H_2O_2]}{k_2[H_2O_2] + k_4[CO] + k_5[RX]}$$

$$\frac{d[RX\cdot]}{dt} = k_5[OH][RX] - k_8[RX][O_2]$$

$$\therefore \quad [RX\cdot]_{ss} = \frac{k_5[OH][RX]}{k_8[O_2]}$$

$$\therefore \quad M = k_4[OH][CO] + nk_5[OH][RX]$$

$$M = [OH](k_4[CO] + nk_5[RX])$$

$$M = \frac{2k_1 I_a[H_2O_2](k_4[CO] + nk_5[RX])}{k_2[H_2O_2] + k_4[CO] + k_5[RX]}$$

Case IV with RX no CO and $k_8 \neq 0$--

$$\frac{d[CO_2]}{dt} = N = nk_8[RX\cdot][O_2]$$

At steady state--

$$\frac{d[OH]}{dt} = 2k_1 I_a [H_2O_2] - k_2[OH][H_2O_2] - k_5[OH][RX] = 0$$

$$[OH]_{ss} = \frac{2k_1 I_a [H_2O_2]}{k_2[H_2O_2] + k_5[RX]}$$

$$\frac{d[RX\cdot]}{dt} = k_5[OH][RX] - k_8[RX\cdot][O_2]$$

$$[RX\cdot]_{ss} = \frac{k_5[OH][RX]}{k_8[O_2]}$$

$$N = nk_5 [OH][RX]$$

$$N = \frac{2k_1 I_a [H_2O_2] n k_5 [RX]}{k_2[H_2O_2] + k_5 [RX]}$$

If these equations are manipulated to eliminate $2k_1 I_a$, the following results are obtained:

$$k_5 = \left(\frac{L}{M} - 1\right) \left(\frac{k_2[H_2O_2]}{k_4[CO]} + 1\right) \frac{k_4[CO]}{[RX]} \text{ when } k_8 = 0$$

$$k_5 = \frac{k_2[H_2O_2]\ (L-M+N) + k_4[CO]\ (L-M)}{(RX)(M-N)} \text{ when } k_8 = 0$$

and $$n = \frac{Nk_4[CO]}{Lk_5\ RX} \left(\frac{k_2[H_2O_2] + k_5\ [RX]}{k_2[H_2O_2] + k_4[CO]}\right.$$

The symbols have the following meanings:
L = Initial CO_2 production rate with only CO in the system.
M = Initial CO_2 production rate with CO + RX in the system.
N = Initial CO_2 production rate with RX but no CO in the system.
In the above equations the following values were used for the rate constant; $k_2 = 8 \times 10^{-13}$ cm^3 $molecule^{-1}$ sec^{-1} and, from Section 4 of this report, $k_4 = 2.69 \times 10^{-13}$ cm^3 $molecule^{-1}$ sec^{-1}. In the well behaved experiments, ($k_8 = 0$), CO_2 production rates were almost, but not quite linear, showing a slight fall off with with time as the experiment progressed. To take the slight curvature into account, the data were "best fitted" using a 2nd degree polynominal and the initial rate determined from the resulting regression equation. In those experiments in which k_8 was not zero, the CO_2 production rate curves showed a slightly more marked curvature with time. These curves were "best fitted" to an experimental equation of the type $y = ae^{bx} + C$. The results of the various experimental determinations are shown in Table 4. The quoted error limits represent the standard deviations of the experimental data points.

CH_3Cl--

Methyl chloride and methyl chloroform were both well behaved systems in that no CO_2 was produced on photolysis of $RX + H_2O_2 + O_2$, or from photolysis of $RX + O_2$. For methyl chloride $k(OH + CH_3Cl) = 3.1 \pm 0.8 \times 10^{-14}$ cm^3 $molecule^{-1}$ sec^{-1} which compares well with values of $4.4 \pm 0.5 \times 10^{-14}$,[9,10] $3.6 \pm 0.8 \times 10^{-14}$[9,10] and $4.6 \pm 0.2 \times 10^{-14}$[9,10] cm^3 $molecule^{-1}$ sec^{-1} obtained in low pressure experiments in the absence of O_2. The agreement is not very good with the value reported by Cox,[29] determined in an air mixture at 1 atm. pressure of 8.5×10^{-14} cm^3 $molecule^{-1}$ sec^{-1}. However, the latter value was only considered good to within a factor of two.[29]

Table 4

SUMMARY OF EXPERIMENTAL DATA FOR THE REACTIONS
OH + HALOCARBONS

Methyl Chloride CH_3Cl

Average System Composition (Torr)

	H_2O_2	H_2O	CO	CH_3Cl	O_2	N_2
without CH_3Cl	0.93	1.61	29.8	0.0	134.2	233.5
with CH_3Cl	0.96	1.59	29.8	59.6	134.1	174.0

Initial CO_2 Production Rates (mole-liter^{-1}sec^{-1} x 10^9)

without CH_3Cl (6 expts) = 0.62, 10.07, 9.47, 9.85, 9.77, 10.25
with CH_3Cl (3 expts) = 8.06, 7.89, 8.47

$k_5 = 3.1 \pm 0.8 \times 10^{-14}$ cm^3 molecule^{-1} second^{-1}

Methyl Chloroform CH_3CCl_3

Average System Composition (Torr)

	H_2O_2	H_2O	CO	CH_3CCl_3	O_2	N_2
without CH_3CCl_3	1.09	1.76	29.8	0.0	134.0	233.4
with CH_3CCl_3	1.09	1.77	29.8	29.8	134.0	203.5

Initial CO_2 Production Rates (mole liter^{-1} sec^{-1} x 10^9)

without CH_3CCl_3 (6 expts) = 16.0, 16.0, 18.0, 16.7, 14.3- 15.4
with CH_3CCl_3 (6 expts) = 13.5, 16.2, 13.6, 15.1, 16.2, 15.6

$k_5 = 2.1 \times 10^{-14}$ cm^3 molecule^{-1} second^{-1}
$k_5 \leq 5.7 \times 10^{-14}$ cm^3 molecule^{-1} second^{-1}

Table 4 (cont.)

Ethyl Chloride C_2H_5Cl

Average System Composition (Torr)

	H_2O_2	H_2O	CO	C_2H_5Cl	O_2	N_2
without C_2H_5Cl	0.00	1.63	29.8	0.0	134.1	233.5
with C_2H_5Cl and CO	1.00	1.63	29.8	29.8	134.1	203.7
with C_2H_5Cl, no CO	0.97	1.59	0.0	29.8	134.1	233.5

Initial CO_2 Production rates (mole liter^{-1} sec^{-1} x 10^9)

without C_2H_5Cl (6 expts) = 18.9, 17.2, 14.9, 17.6, 17.3, 17.1
with C_2H_5Cl and CO (4 expts) = 14.3, 13.3, 15.2, 13.8
with C_2H_5Cl, no CO (4 expts) = 11.6, 10.2, 12.4, 11.5

$k_5 = 4.4 \pm 2.5 \times 10^{-13}$ cm^3 molecule^{-1} second^{-1}
$nk_5 = 2.8 \pm 1.5 \times 10^{-13}$ cm^3 molecule^{-1} second^{-1}

1,2-Dichloroethane CH_2ClCH_2Cl

Average System Composition (Torr)

	H_2O_2	H_2O	CO	CH_2ClCH_2Cl	O_2	N_2
without CH_2ClCH_2Cl	1.02	1.68	29.8	0.0	134.1	233.4
with CH_2ClCH_2Cl and CO	1.02	1.67	29.8	29.8	134.1	203.6
with CH_2ClCH_2Cl, no CO	1.00	1.64	0.0	29.8	134.1	238.5

Initial CO_2 Production Rates (mole liter^{-1} sec^{-1} x 10^9)

without CH_2ClCH_2Cl (5 expts) = 9.9, 9.7, 10.7, 10.7, 11.1
with CH_2ClCH_2Cl and CO (6 expts) = 9.7, 12.2, 11.8, 11.7, 9.9, 9.5
with CH_2ClCH_2Cl, no CO (5 expts) = 8.5, 9.0, 9.4, 8.5

$k_5 = 6.5 \times 10^{-14}$ cm^3 molecule^{-1} second^{-1}
$k_5 \leq 2.9 \times 10^{-13}$ cm^3 molecule^{-1} second^{-1}
$nk_5 = 7.1 \times 10^{-14}$ cm^3 molecule^{-1} second^{-1}
$nk_5 \leq 2.4 \times 10^{-13}$ cm^3 molecule^{-1} second^{-1}

Table 4 (cont.)

Methylene Chloride CH_2Cl_2

Average System Composition (Torr)

	H_2O_2	H_2O	CO	CH_2Cl_2	O_2	N_2
without CH_2Cl_2	0.93	1.52	29.8	0.0	134.2	233.6
with CH_2Cl_2 and CO	0.93	1.52	29.8	59.6	134.2	174.0
with CH_2Cl_2 no CO	0.94	1.54	0.0	59.6	134.2	203.7

Initial CO_2 Production Rates (mole $liter^{-1}$ sec^{-1} x 10^9)

without CH_2Cl_2 (6 expts) = 9.62, 10.07, 9.47, 9.85, 9.77, 10.25
with CH_2Cl_2 and CO (4 expts) = 8.54, 8.33, 9.20, 8.03
with CH_2Cl_2 no CO (2 expts) = 0.81, 1.08

$k_5 = 2.7 \pm 1.0 \times 10^{-14}$ cm^3 $molecule^{-1}$ $second^{-1}$
$nk_5 = 3.5 \pm 1.1 \times 10^{-15}$ cm^3 $molecule^{-1}$ $second^{-1}$

Chloroform $CHCl_3$

CO_2 was produced from the reaction $CHCl_3 + OH + O_2$ and the photolysis of $CHCl_3 + O_2$. The second calculation method was used and corrected for photolysis.

Average System Composition (Torr)

	H_2O_2	H_2O	CO	$CHCl_3$	O_2	N_2
Without $CHCl_3$	1.16	1.90	29.8	0.0	134.0	233.1
With $CHCl_3$ and CO	1.14	1.87	29.8	59.6	134.0	173.6
With $CHCl_3$, no CO	1.16	1.89	0.0	59.6	134.0	203.4
Photolysis of $CHCl_3$	0.00	0.00	0.0	59.6	134.0	203.4

Initial CO_2 Production Rates x 10^9 (mole-$liter^{-1}$-$second^{-1}$)

Without $CHCl_3$ (2 expts.) = 10.24, 8.03
With $CHCl_3$ and CO (2 expts.) = 9.71, 9.05
With $CHCl_3$, no CO (2 expts.) = 4.69, 3.08
Photolysis of $CHCl_3$ (2 expts.) = 0.59, 0.16

$k_5 = 1.4 \times 10^{-14}$ cm^3-$molecule^{-1}$-$second^{-1}$
$k_5 \leq 5.0 \times 10^{-14}$ cm^3-$molecule^{-1}$-$second^{-1}$
$n = 0.74$

These results were calculated after making a correction for photolysis in the $CHCl_3 + O_2$ system.

It has recently been suggested[32] that one of the channels for reaction of CH_2Cl, formed by the attack of OH on CH_3Cl, in air, is as follows; $CH_2Cl + O_2 \rightarrow CH_2ClO_2$ followed by either, $2CH_2ClO_2 \rightarrow 2CH_2ClO + O_2$ and or $CH_2ClO_2 + HO_2 \rightarrow CH_2ClO + OH$. The present results indicate that the latter reaction channel cannot be very important, since if it were, it would result in $k(OH + CH_3Cl)$ obtained in our system being lower than the reported values.

CH_3CCl_3--

The precision of the data for methyl chloroform was not as good as for methyl chloride. This was largely due to the relatively low vapor pressure of CH_3CCl_3 preventing an optimum pressure of the gas being used in the reaction mixture. An unfortunate characteristic of the competitive rate method requires that for optimum precision L = 2M using the nomenclature defined earlier. For reactions, (OH + RX), with relatively low rates compared to CO + OH, optimum precision requires relatively high pressures of RX. Because of this difficulty, the rate constant for $k(OH + CH_3CCl_3) = 2.1 \times 10^{-14}$ cm^3 $molecule^{-1}$ sec^{-1} is quoted as the most probable value, with a limit of $k \leq 5.7 \times 10^{-14}$ cm^3 $molecule^{-1}$ sec^{-1}. These values are in accord with those in the literature of $1.64 \pm 0.2 \times 10^{-14}$[29] 2.19×10^{-14},[31] $1.5 \pm 0.3 \times 10^{-14}$[9,10] and 2.8×10^{-14}[29] cm^3 $molecule^{-1}$ sec^{-1}.

The next three compounds, C_2H_5Cl, CH_2ClCH_2Cl and CH_2Cl_2, were not well behaved in so much that CO_2 was generated in the reactions $RX + H_2O_2 + O_2$ on photolysis, though not in the reaction $RX + O_2$ on photolysis. Experiments were therefore made to determine initial CO_2 production rates for $RX + H_2O_2 + O_2$ on photolysis, in addition to the usual required CO_2 production rate determinations.

C_2H_5Cl--

The value of $k(OH + C_2H_5Cl) = 4.4 \pm 2.5 \times 10^{-13}$ cm^3 $molecule^{-1}$ sec^{-1} calculated from equation 2, is in good agreement with the only other literature reference of $3.9 \pm 0.7 \times 10^{-13}$ cm^3 $molecule^{-1}$ sec^{-1}.[31]

$ClCH_2CH_2Cl$--

The precision of the results for 1,2 dichloroethane, were not very good, largely due to the similar reaction rates in the presence and absence of RX in the reaction mixture. A most probable value of $k(OH + CH_2ClCH_2Cl) = 6.5 \times 10^{-14}$ cm^3 $molecule^{-1}$ sec^{-1} was derived with an upper limit of $k(OH + CHClCH_2Cl) \leq 2.9 \times 10^{-13}$ cm^3 $molecule^{-1}$ sec^{-1}. The latter is in satisfactory agreement with the only other literature value, of $k(OH + CH_2ClCH_2Cl) = 2.2 \pm 0.5 \times 10^{-13}$ cm^3 $molecule^{-1}$ sec^{-1}.

CH_2Cl_2--

The CO_2 production rates in the methylene chloride system, $CH_2Cl_2 + OH + O_2$ showed a pronounced upward curvature after about 2-3 minutes of reaction indicating the possibility of a chain reaction. However, the initial CO_2 production rate was only about 10% of that in the $CH_2Cl_2 + OH + O_2 + CO$ reaction. The rate was considerably less than in the C_2H_5Cl and $C_2H_4Cl_2$ experiments, and the CO_2 versus time plots for the $CH_2Cl_2 + OH + O_2 + CO$ system, only showed a very slight upward curvature. The derived rate constant $k(OH + CH_2Cl_2) = 2.7 \pm 1.0 \times 10^{-14}$ cm^3 $molecule^{-1}$ sec^{-1} was not in good agreement with literature values of $1.45 + 0.2 \times 10^{-13}$,[25] $1.55 \pm 0.34 \times 10^{-13}$[9,10] and 1.04×10^{-13} cm^3 $molecule^{-1}$ sec^{-1}, the latter being obtained in an experiment with air at 1 atm pressure. It is not obvious why the present result differs from the literature values. Impurities were detected chromatographically in our CH_2Cl_2 sample prior to purification, but were all absent after treatment. In two of the literature studies, CH_2Cl_2 purities were

assigned at 99.93%[9,10] and 99.9%[25] and it seems unlikely that ~0.1% of a likely impurity could account for the order of magnitude difference in reaction rates. A possible explanation lies in the reaction mechanism involved. The primary OH attack on CH_2Cl_2 is that of H abstraction, $CH_2Cl_2 + OH \rightarrow CHCl_2 + H_2O$. In the presence of oxygen, the $CHCl_2$ radical can react with O_2 to presumably form $CHCl_2O_2$[32] which then decomposes as; $CHCl_2O_2 \rightarrow COCl_2 + HO$. Alternatively one could write, $CHCl_2 + O_2 = COCl_2 + OH$ directly, for which it is easily possible to show the reaction is highly exothermic. Previously it had been postulated[32] that $CHCl_2O_2$ decomposes to ClO and HCOCl, though this interpretation caused some difficulties since no HCOCl was observed in the experimental system. If the reaction channel $CHCl_2 + O_2 \rightarrow COCl_2 + OH$, is a significant path for the destruction of $CHCl_2$, then indeed this would result in our method giving a low value for $k(OH + CH_2Cl_2)$, since the CH_2Cl_2 is effectively not competing with CO for the available OH. Alternatively if $CHCl_2O_2 \rightarrow HCOCl + ClO$ is an important channel, then a low value could also result if the reaction $CO + ClO \rightarrow CO_2 + Cl$ takes place readily. To date, there do not appear to be any data on this reaction.

In those reactions in which CO_2 is produced due to $RX + OH + O_2 \rightarrow CO_2 +$ product, it is possible to calculate values of n for the process from the expression;

$$n = \frac{Nk_4[CO]}{k_5L[RX]} \quad \frac{k_2[H_2O_2] + k_5[RX]}{k_2[H_2O_2] + k_4[CO]}$$

where the symbols have the values defined earlier. Values so obtained are as follows; 0.63, 1.09 and 0.13 for C_2H_5Cl, $C_2H_4Cl_2$ and CH_2Cl_2, respectively. That n for the $C_2H_4Cl_2$ reaction is >1 simply implies that it is possible for both carbon atoms to be converted to CO_2 in the reaction, though within

the precision of the data the value of 1.09 is hardly significant. Recently, a study of the reaction products formed when C_2H_5Cl and $C_2H_4Cl_2$ are subject to H atom abstraction in air has been made (private communication from P. L. Hanst and J. W. Spence). CO_2 was found to constitute $\simeq$60 and 50 mole %, respectively of the product for C_2H_5Cl and $C_2H_4Cl_2$, in good agreement with the values reported here.

Detailed experiments were not made on $CHCl_3$, C_2Cl_4, and $C_2H_4Br_2$ for a variety of reasons.

$CHCl_3$--

Preliminary experiments made with this compound indicated several difficulties. Irradiation of the system, $CHCl_3 + O_2$ alone resulted in the production of CO_2, with an initial rate about 10% of that in the $CHCl_3 + OH + CO + O_2$ experiments. CO_2 was also produced in relatively large amounts in the $CHCl_3 + OH + O_2$ system. The results of these preliminary experiments are shown in Table 4. Only two experiments were made for each set of experimental conditions. The most probable value of $k(CHCl_3 + OH) = 1.4 \times 10^{-14}$ cm^3 molecule^{-1} sec^{-1} is not in good agreement with the only other literature value of $1.01 \pm 0.15 \times 10^{-13}$ cm^3 molecule^{-1} sec^{-1}.[9] If the latter value is indeed correct, the low value obtained in this study requires the presence of some species in the system capable of oxidizing CO to CO_2. Spense, Hanse and Gay[32] have postulated the OH attach on $CHCl_3$ in the presence of O_2 leads to the formation of CCl_3O_2 which then decomposes to $COCl_2 + ClO$. If the reaction $ClO + CO$ is rapid, this could account for our low value of $k(OH + CHCl_3)$. To date, there do not appear to be any data on the kinetics of the $CO + ClO$ reaction. The value of n reported in Table 4 implies that 74% of the chloroform "ends up" as CO_2, this finding is at odds with that of Hanst et al., which suggests that the major product is $COCl_2$. However, in view of the problems associated with this determination it is doubtful if much weight

can be assigned to these results.

C_2Cl_4--

Preliminary experiments with this system indicated that large amounts of CO_2 were produced from the system C_2Cl_4 + OH + O_2. Since fairly comprehensive data were already available for the C_2Cl_4 + OH reaction it was decided not to pursue the study further.

$C_2H_4Br_2$--

The system $C_2H_4Br_2$ + O_2 produced substantial amounts of CO_2 on irradiation. For this reason no attempt was made to study the $C_2H_4Br_2$ + OH reaction rate.

KINETIC RESULTS USING THE DYNAMIC REACTOR

Introduction

The primary goal of this phase of the project was to determine the rates of reaction of various halocarbons with hydroxyl radicals. A competitive rates method was used as described in the previous section in which the rate of an unknown reaction is determined by comparison with a well known reaction in which it is in competition. The main difference in the present case was the use of a flow, rather than a static reactor with mass spectrometric rather than gas chromatographic detection of products.

The source of hydroxyl radicals was the photolytic decomposition by 2537Å light of hydrogen peroxide;

$$H_2O_2 + h\nu \longrightarrow 2OH$$

This reaction has been extensively studied by Volman[33] and produces a clean source of hydroxyl radicals in the electronic ground state without the complication of any other interferring radicals or excited molecules. The competing reactions are:

$$OH + CO \xrightarrow{k_1} CO_2 + H$$

and

$$OH + RX \xrightarrow{k_2} P_2$$

where RX is a chlorinated hydrocarbon and P_2 is an unidentified product. The requirements for use of this competitive rate technique are that the OH radicals must react only with the CO and RX and that no other sources of CO_2 are present. This latter requirement played an important role in some of the studies.

The rates of formation of the products of the two reactions are given by:

$$\frac{d[CO_2]}{dt} = R_{CO_2} = k_1 [CO][OH] \qquad 1$$

$$\frac{d[P_2]}{dt} = R_{P_2} = k_2 [RX][OH] \qquad 2$$

Taking the ratio of these two rates;

$$\frac{R_{CO_2}}{R_{P_2}} = \frac{k_1 [CO][OH]}{k_2 [RX][OH]} \qquad 3$$

$$\frac{[RX]}{[CO]} = \frac{k_1}{k_2} \frac{R_{P_2}}{R_{CO_2}} \qquad 4$$

If $R^*_{CO_2}$ is defined as the rate of formation of CO_2 in the absence of competing reactant, then;

$$R_{CO_2} = R^*_{CO_2} - R_{P_2} \qquad 5$$

defines the rate of formation of CO_2 in the presence of a competing reactant, R_2. Rearranging 5,

$$R_{P_2} = R^*_{CO_2} - R_{CO_2} \qquad 6$$

and substituting into 4, we have;

$$\frac{[R_2]}{[CO]} = \frac{k_1}{k_2} \quad \frac{R^*_{CO_2} - R_{CO_2}}{R_{CO_2}}$$

or

$$\frac{[R_2]}{[CO]} = \frac{k_1}{k_2} \quad \frac{R^*_{CO_2}}{R_{CO_2}} - 1 \qquad 7$$

Equation 7 is the form of the rate expression used to compare the two rates, k_1 and k_2.

The experimental method is as follows. A flow of gases containing H_2O_2, CO and a carrier gas (air, O_2 or He) is set up. The H_2O_2 and CO concentrations may be determined absolutely or simply as known gas flow rates. The 2537Å lamps are turned on and the rate of formation of CO_2, $R^*_{CO_2}$, determined for a given flow rate of reactants. Without changing any of the initial gas flow rates, a small amount of chlorinated hydrocarbon is added to the reactant gas stream. The 2537Å lamps are again turned on and the new rate of formation of CO_2 determined, R_{CO_2}. The flow rate of chlorinated hydrocarbon may be changed and the rate of formation of CO_2 determined for this new condition. This

procedure is repeated for the desired number of points.

Each set of data points yields a ratio of the rate constants, k_1/k_2 versus RX concentration. Since k_1 is well known, k_2 can be accurately determined.

Apparatus

A diagram of the apparatus used in these experiments is shown in Figure 4. The carrier gas was either helium, nitrogen, oxygen or air. All were tried with various degrees of success. Matheson Research Grade CO was added directly to the carrier gas flow. Part of the carrier gas was diverted and bubbled through a reservoir of H_2O_2 immersed in a thermostated bath held slightly below ambient temperature to prevent condensation. The two flows were recombined prior to entering the quartz reactor. A pyrex mixing tube allowed the gases to be transported to the lower end of the quartz reactor which was positioned in the center of an RPR-16 Rayonet Photochemical Reactor with 16, 2537Å mercury lamps. The gases entered the reactor where they were irradiated. The reacted gases then entered a second manifold, shown in Figure 5. A 9" capillary tube was used to sample these reacted gases into the first differentially pumped stage of the mass spectrometer. The gases then passed through two stages of differential pumping before entering the ion region of an Extranuclear quadrupole mass spectrometer using electron impact ionization with phase sensitive detection using a Daley detector.

Experimental Method

A typical experiment was conducted in the following manner. First, a known flow of CO, H_2O_2 and carrier gas was established. Once the flow of gases had stabilized, the photolysis lamps were turned on and the amount of CO_2 formed determined. The latter was not determined absolutely but as a linear pen deflection on a chart recorder with the mass spectrometer locked on mass 44.

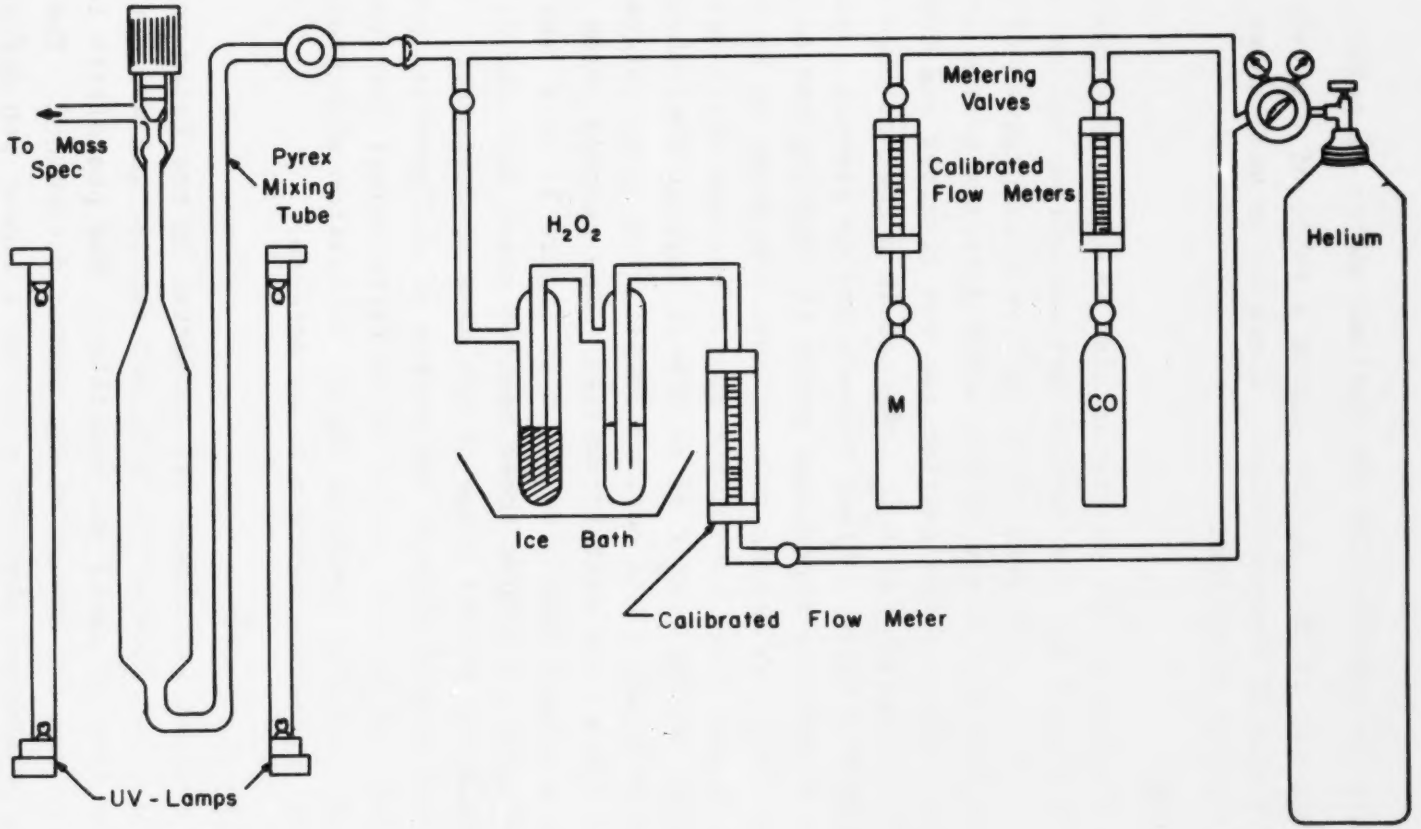

Figure 4. Gas Flow and Reactor System

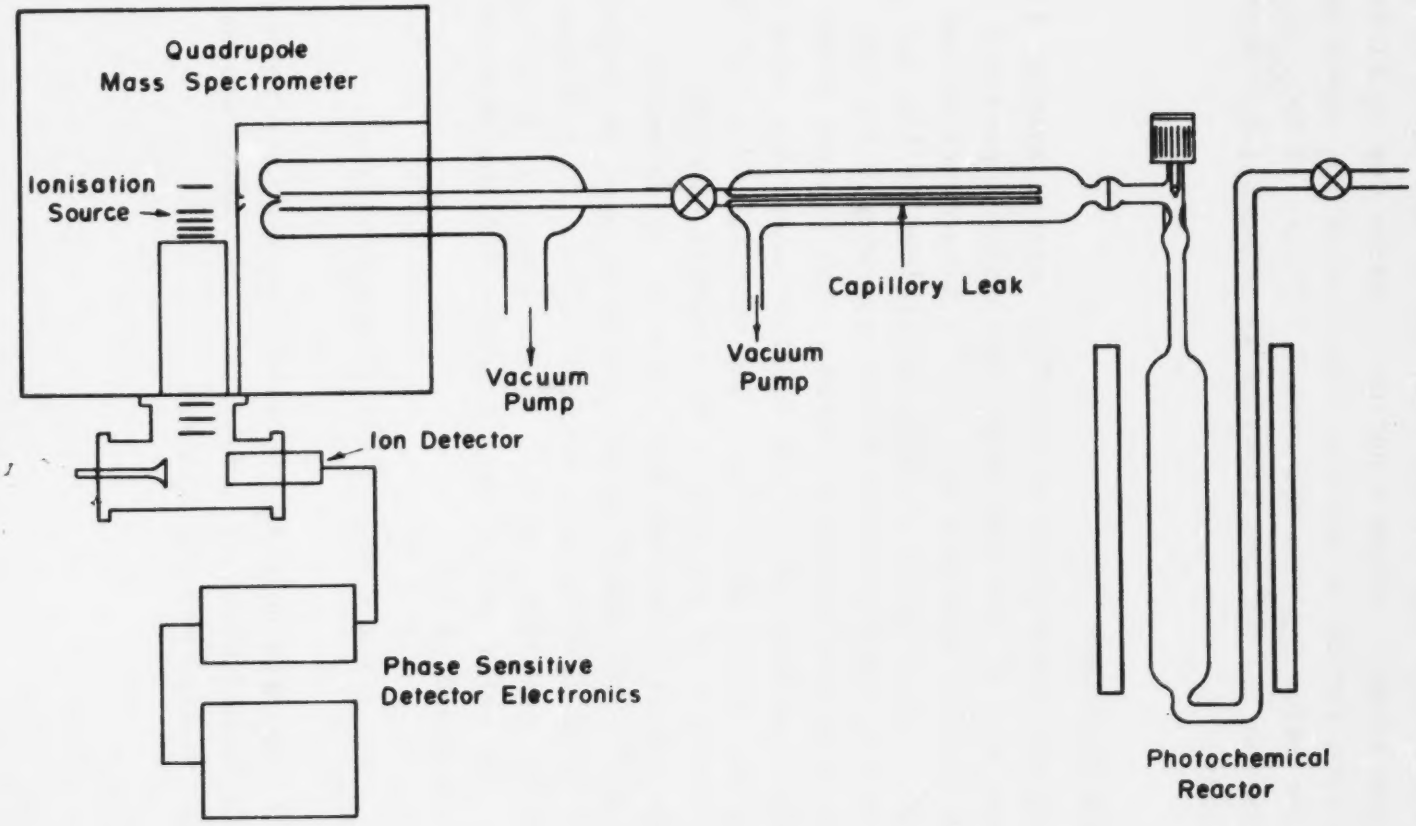

Figure 5. Mass Spectrometric Gas Sampling System

This was the value of $R^*_{CO_2}$ in equation 7.

The lamps were then turned off, and RX was added to the reactant gas stream. After a period to allow for equilibrium, the lamps were turned on and the formation of CO_2 again measured. This was the value R_{CO_2} in equation 7. Values of $R^*_{CO_2}/R_{CO_2}$ were determined for various flows of RX in equation 7 with CO kept constant.

Results

Calibration Technique--

During the development of the flow reactor system, a paper by Heicklen, et. al. was published indicating a pressure dependence for the reaction OH + CO.[14] Literature values for the OH + CO, rate constant, mainly determined in the low pressure region, were felt not to be trustworthy for the atmospheric pressure conditions used in the present study. An independent determination of the reaction under our experimental conditions was deemed necessary. The reaction OH + C_2H_6 had been well studied; it appears to be a simple hydrogen abstraction reaction and had been shown to be pressure independent.[34] This reaction was therefore used to determine a suitable value for the rate constant of the CO + OH reaction at atmospheric pressure. A plot of these data is presented in Figure 6. The value of the rate constant for the OH + CO reaction was found to be;

$$k_{OH + CO} = 3.1 \pm 0.5 \times 10^{-13} \text{ cm}^3/\text{molecule-sec}$$

This result supports Heicklein's assertion that the OH + CO reaction is indeed pressure dependent. This value was used throughout the flow reactor studies.

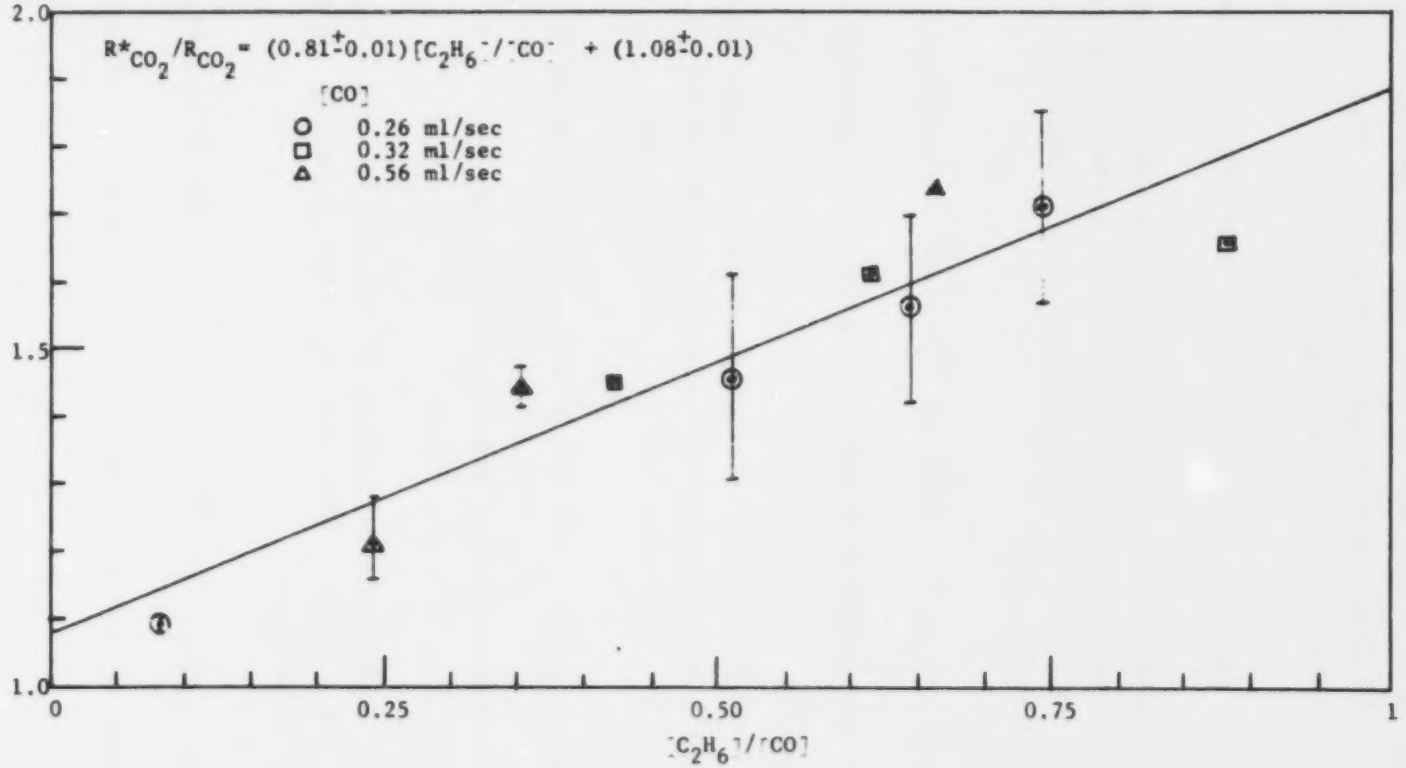

Figure 6. Plot of Data for OH + Ethane. Reaction at 760 Torr and 298°C

$OH + CH_3Cl$--

The first reaction studied was the reaction of $OH + CH_3Cl$. The data obtained is plotted in Figure 7. The rate constant determined for this reaction was

$$k_{OH + CH_3Cl} = 4.6 \pm 0.7 \times 10^{-14} \text{ cm}^3/\text{molecule.sec}$$

The temperature dependence of this reaction over the range 10 to 90°C was also investigated. An Arrhenius plot of the data is shown in Figure 8 and the temperature dependent rate constant was determined to be;

$$k_{OH + CH_3Cl} = 1.68 \times 10^{-12} e^{\frac{-2111}{RT}} \text{ cm}^3/\text{molecule.sec}$$

in good agreement with the two previously reported values.

$OH + CH_3CCl_3$--

A purified sample of methyl chloroform was used in this investigation. The data obtained for this reaction is plotted in Figure 9. The rate constant obtained was;

$$k_{OH + CH_3CCl_3} = 1.6 \pm 0.2 \times 10^{-14} \text{ cm}^3/\text{molecule.sec}$$

in good agreement with the literature values.

$OH + CHCl_3$--

An inhibitor free sample of chloroform was obtained and used in this study. The data obtained is shown in Figure 10. The rate constant;

$$k_{OH + CHCl_3} = 1.16 \pm 0.15 \times 10^{-13} \text{ cm}^3/\text{molecule.sec}$$

is in good agreement with existing literature values.

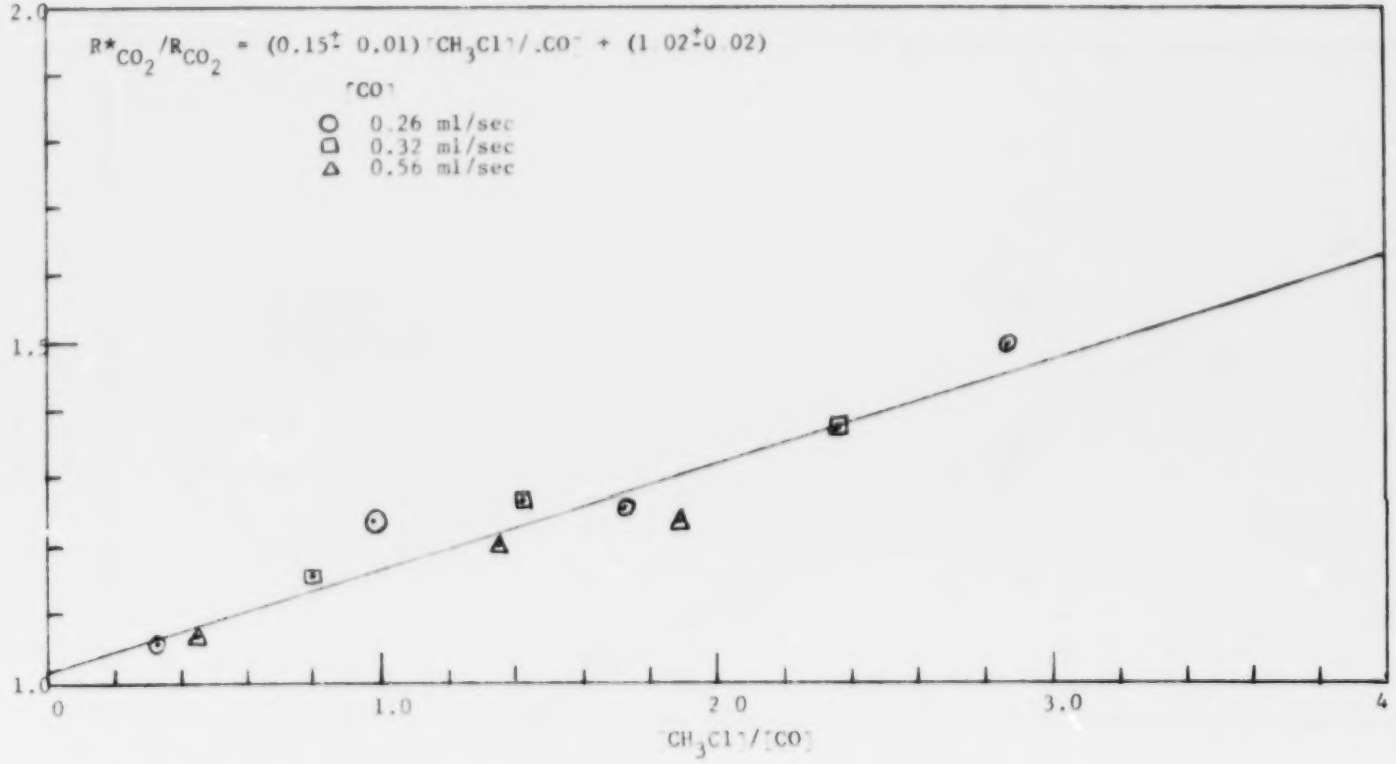

Figure 7. Plot of Data for OH + Methylchloride. Reaction at 760 Torr and 298°C

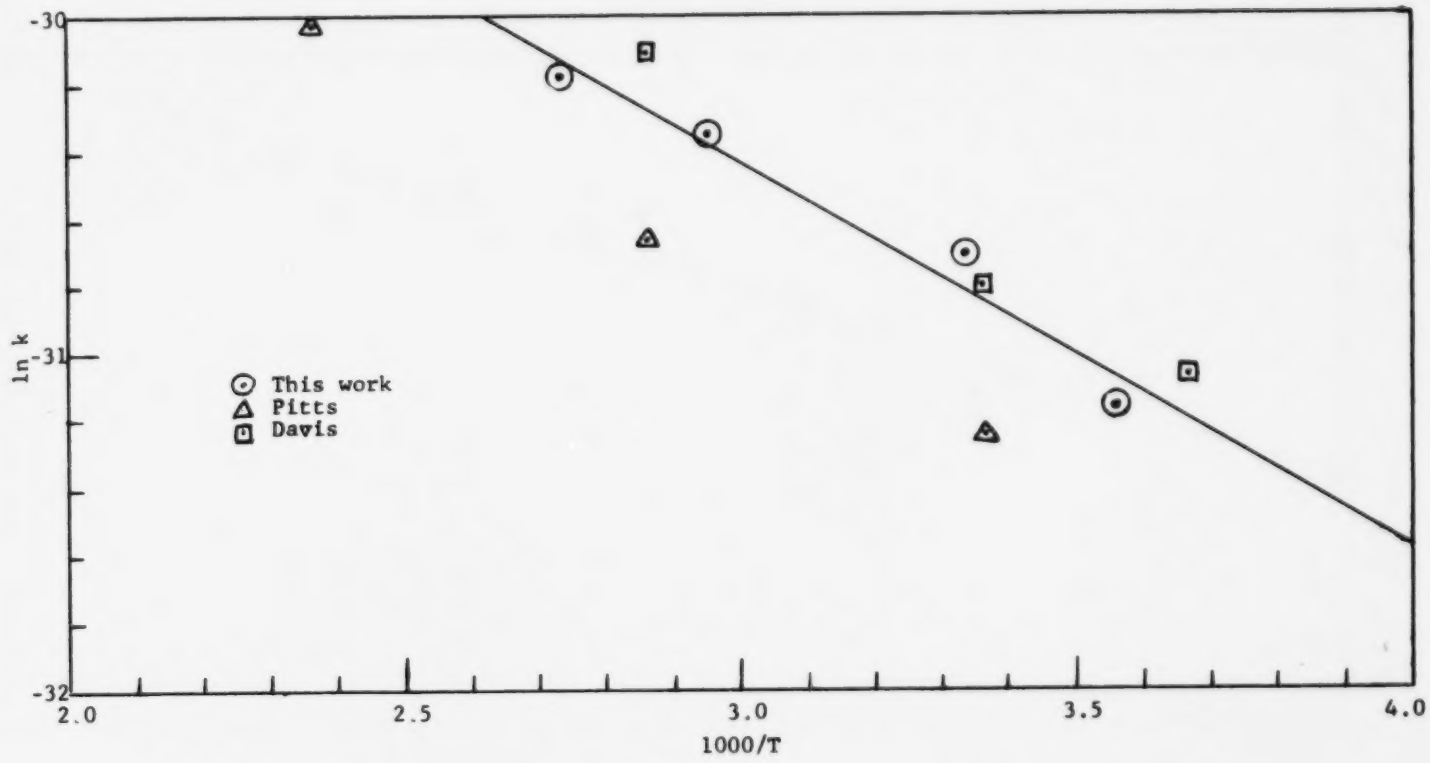

Figure 8. Temperature Dependence of the Reaction OH + CH_3Cl

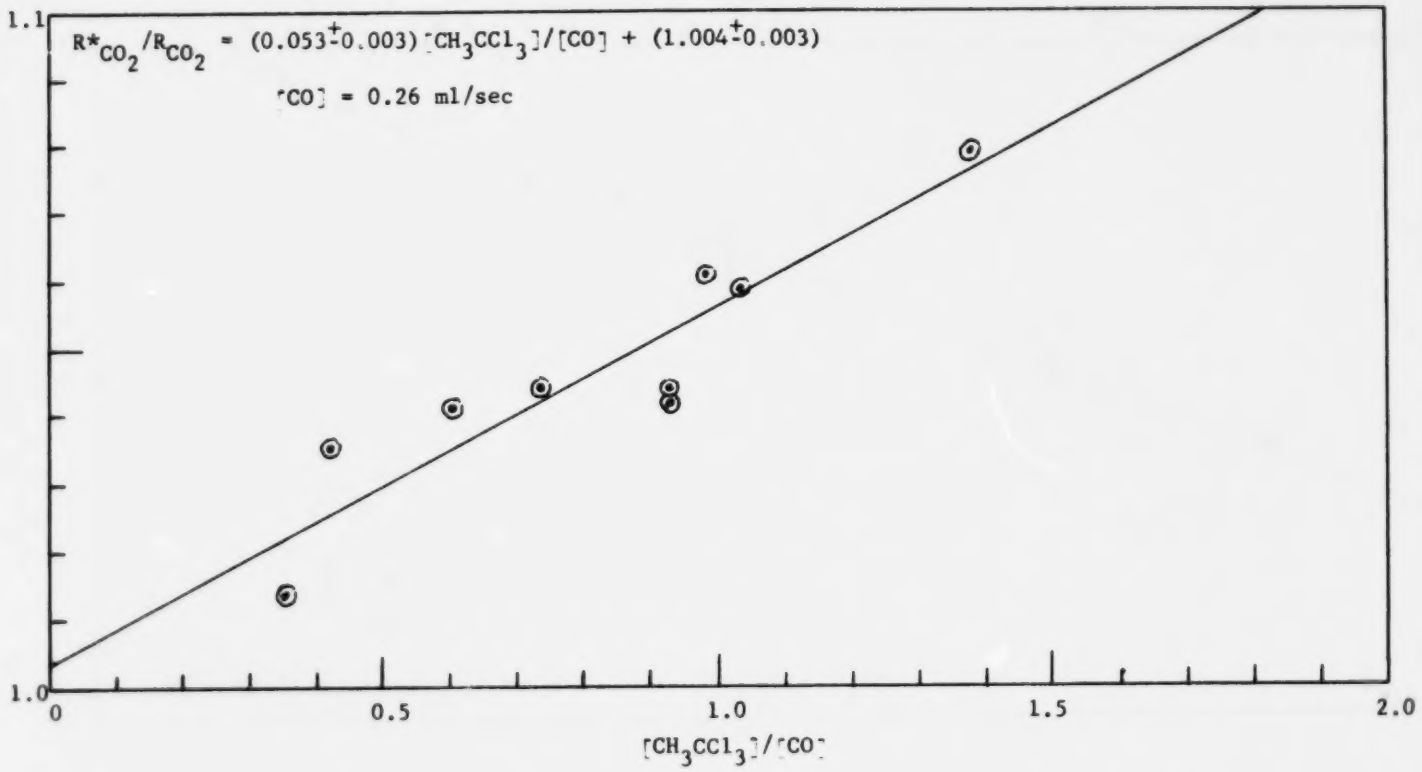

Figure 9. Plot of Data for OH + Methylchloroform. Reaction at 760 Torr and 298°C

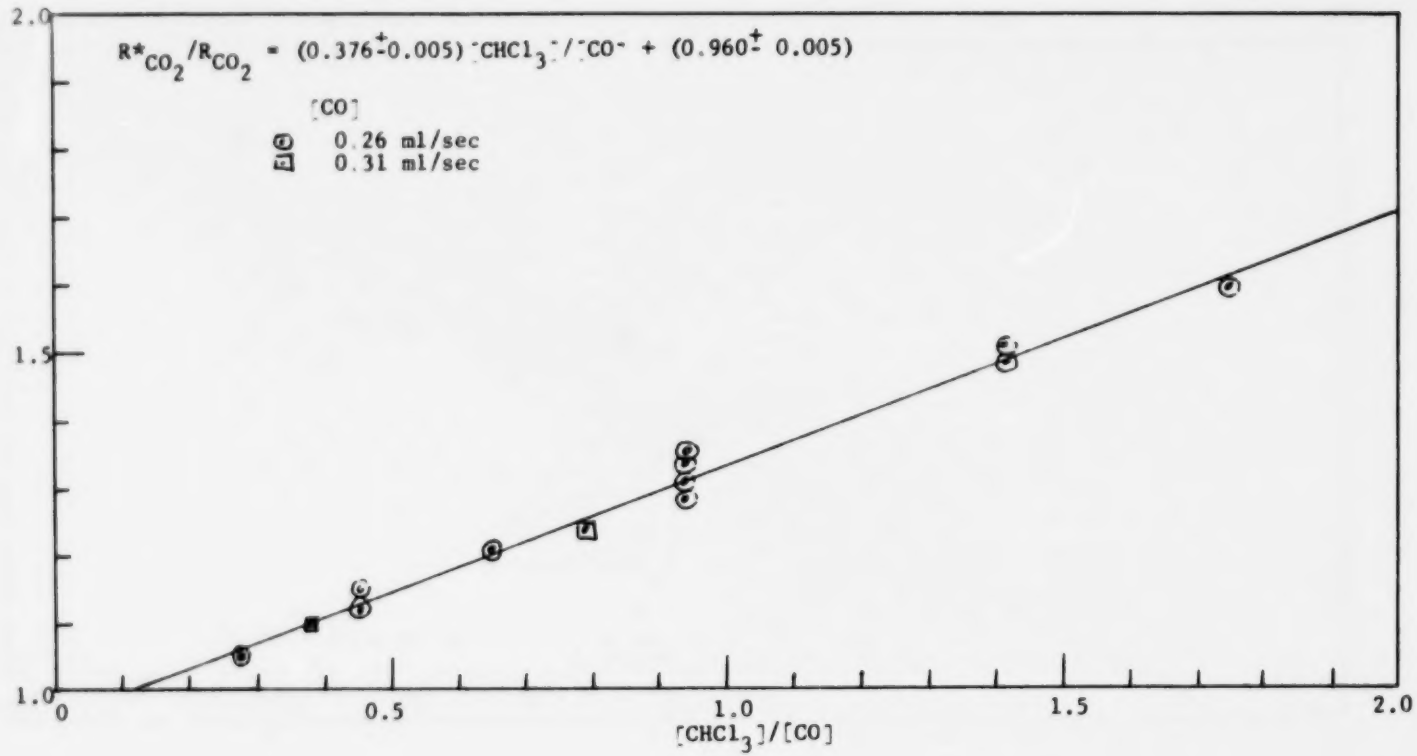

Figure 10. Plot of Data for OH + $CHCl_3$. Reaction at 760 Torr and 298°C

$OH + CH_2Cl_2$--

Methylene chloride was the last compound investigated by the flow reactor technique. The data obtained is plotted in Figure 11. The value obtained for the rate constant;

$$k_{OH + CH_2Cl_2} = 1.46 \pm 0.19 \times 10^{-13} \text{ cm}^3/\text{molecule.sec}$$

is in fair agreement with previous literature values.

Discussion of Results

Completed Systems--

As can be seen from Table 5, the data obtained on the systems studied are in excellent agreement with previous literature values. The contribution made by this study was to confirm the reliability of these rate constants under conditions more closely resembling tropospheric conditions.

Problems with the Technique--

The flow reactor technique was designed to be simple and yet yield pertinent data regarding the tropospheric reactivity of various halocarbons with hydroxyl radicals. This was the first time an attempt to carry out these reactions was made in the presence of air at 760 torr and ambient temperatures. However, as with many such systems, side reactions occurred which prevented the use of this technique for the measurement of the kinetics of all the halocarbons desired. Previously it was stated that a requirement of the successful application of this technique was that no other sources of CO_2 should exist. Unfortunately, the conditions under which these reactions were conducted resulted in the production of large amounts of CO_2 from the reaction of OH with some of the halocarbons. Only in the four systems reported was the production of CO_2 by unwanted reaction low enough or completely absent that the technique could be used satisfactorily. All other systems

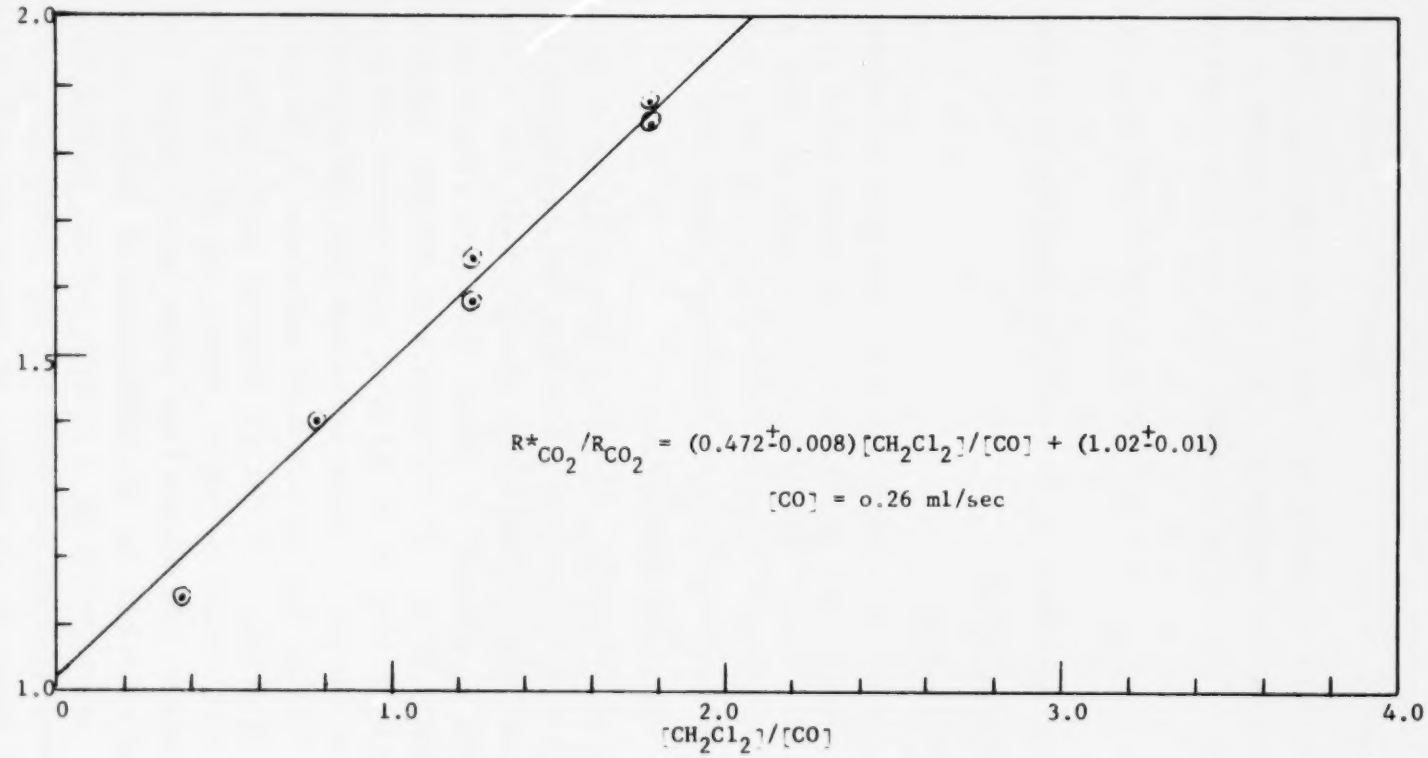

Figure 11. Plot of Data for OH + Methylene Chloride. 760 Torr and 298°C

Table 5

SUMMARY OF RATE DATA FOR SELECTED HALOCARBONS

Compound	$k \times 10^{14}$ cm^3 $Molecule^{-1}$ sec^{-1}	$A \times 10^{12}$ cm^3 $molecule^{-1}$ sec^{-1}	E Cal.	Source	$k_{298°K}$ (selected) $\times 10^{14}$ cm^3 $molecule^{-1}$ sec^{-1}	$k_{265°K}$ (selected) $\times 10^{14}$ cm^3 $molecule^{-1}$ sec^{-1}
CH_3Cl	4.4 ± 0.5	-.1	2700	Pitts[25]		
	3.6 ± 0.8			Howard[9]		
	4.3	1.84	2181	Davis[30]		
	8.5			Cox[29]	4.2	2.6
	3.1 ± 0.8			IITRI[(a)]		
	4.6 ± 0.7	1.68	2211	IITRI[(b)]		
CH_2Cl_2	14.5 ± 2.0			Pitts		
	15.5 ± 3.4			Howard		
	11.3 ± 0.6	4.27	2174	David	13.8	9.0
	10.4			Cox		
	2.7 ± 1[(d)]			IITRI		
$CHCl_3$	10.1 ± 1.5			Howard		
	16.8			Cox		
	10.4 ± 1.2	4.69	2254	David	11.1	7.3
	≤ 5.0			IITRI		
	11.6 ± 1.5			IITRI[(b)]		
C_2H_5Cl	39 ± 7.0			Howard	40.2	26.3
	44 ± 25			IITRI		
CH_2ClCH_2Cl	22.0 ± 5.0			Howard	19.1	12.5
	6.5 ($\leq$29)			IITRI		
CH_3CCl_3	1.5 ± 0.3			Howard		
	1.59 ± 0.16	3.72	1627	David		
	2.19 ± 0.27	1.95	1331	Kaufman[32]	1.7	1.2
	2.8			Cox		
	2.1 ($\leq$5.7)			IITRI		
	1.6 ± 0.2			IITRI[(b)]		

a) IITRI Static Reactor b) IITRI Flow Reactor

d) This value is known to be incorrect and was not considered in deriving k (selected).

produced more CO_2 than the reference reaction OH + CO. This revelation was disappointing since it precluded further use of this technique.

IMPLICATIONS WITH RESPECT TO ATMOSPHERIC LIFETIMES OF THE KINETICS OF THE OH + HALOCARBON REACTIONS

Introduction

The overall objective of the preceding kinetic studies is to allow estimates to be made of the likely tropospheric lifetimes of the halocarbon species studied. In making such a calculation it is assumed that the only sink for these species in the troposphere is attack by OH radicals. To date, this is the only known sink. The tropospheric lifetime for the halocarbon species is given by;

$$\tau_e \text{ (tropospheric lifetime)} = [k_i[OH]_{ave}]^{-1}$$

In this expression k_i is the bimolecular rate constant for the halocarbon + hydroxyl reaction, RX_i + OH → Products, and $[OH]_{ave}$ is the average OH concentration. Both these quantities are averaged over their geographic, altitude, diurnal and seasonal variation. Of these latter variables, the only one with an effect on the rate constant k_i is the temperature variation with altitude. The best values to be assigned to k_i and $[OH]_{ave}$ will now be considered.

Evaluation of the Kinetic Data

In Table 5 all the currently available data on the rate constants for the RX_i + OH reactions studied in this investigation are presented. A value of k (selected) was obtained by weighting the various values in proportion to their assigned error. The temperature dependence of the rate constant has been determined for CH_3Cl, CH_2Cl_2, $CHCl_3$ and CH_3CCl_3. For the purpose of the calculations a weighted average tropospheric

temperature 265°K is assumed,[30] and the rate constants at 265°K were calculated based on the quoted activation energies. For the halocarbons for which the temperature dependency of the rate constant was not known, an activation energy of 2.07 kcal was assumed based on a simple average of the values shown in Table 5.

Tropospheric OH Radical Concentration

The value to be used for $[OH]_{ave}$ is somewhat uncertain. Several attempts to measure OH radical concentrations in the troposphere have been reported.[35-37] Measured concentrations have ranged from 16 to $< 4 \times 10^6$ molecule cm^{-3}, the lower detection limit of the experimental method. In one case, a high value of $\lesssim 1.5 \times 10^8$ molecule cm^{-3} was reported. Prior to these measurements, estimates of the tropospheric OH radical concentration had been made based largely on the then known chemistry of the atmosphere in terms of sources and sinks for the trace gas species. Values in the range $3\text{-}6 \times 10^6$ molecule cm^{-3} were quoted for yearly average concentrations. More recently lower values have been proposed; $\sim 7 \times 10^5$ molecule cm^{-3} based on the atmospheric CO distribution[38] (this estimate was made before the pressure dependence of the CO + OH reaction was established which would have the effect of decreasing further this estimate) and $2\text{-}6 \times 10^5$ molecule cm^{-3} based on the halocarbon sources, sinks and atmospheric abundances.[8,39]

In summary, although two direct measurements have been made of OH radical atmospheric concentrations in which relatively high values of [OH] were reported, there appears to be a body of evidence developing which strongly suggests that concentrations in the range $2\text{-}6 \times 10^5$ molecule cm^{-3} are probably close to reality and will be assumed in the following calculations.

Halocarbon Tropospheric Lifetimes

The results of the tropospheric lifetime calculations based on the above rate constants and OH radical concentrations are shown in Table 6. It is instructive to compare the computed lifetime in Table 6 with those obtained from measurements of CH_3CCl_3 and $CHCl_3$ emissions, and present atmospheric loading. Values of 7.2 ± 1.2 and 1.7 ± 0.4 years, respectively, were obtained for CH_3CCl_3 and $CHCl_3$.[8,39] These values are in fair agreement with those calculated in Table 6 suggesting an average OH radical concentration of the order of $\sim 4 \times 10^5$ molecule cm^{-3} in good agreement with the latest estimates.[38,39]

Generally if the tropospheric lifetime of a chemical species is 10 years or less,[30] its flux into the stratosphere is reduced to 10% or less of the total ground level emissions. With the possible exception of CH_3CCl_3, it appears that none of the halocarbons listed in Table 5 will contribute significantly to the stratospheric chlorine burden as intact halocarbons. Even for CH_3CCl_3, at its present levels in the atmosphere, 98.8 ± 9.7 ppt (v/v),[8] it is doubtful that it could contribute any more chlorine to the stratosphere than CH_3Cl which is present, largely from natural sources in the troposphere, at 713 ± 51 ppt (v/v).[8] However, if emissions of CH_3CCl_3, which it seems have been established as entirely anthropogenic in origin, were to continue to increase, this compound could possibly become a cause for concern.

Table 6

CALCULATED TROPOSPHERIC LIFETIMES

Compound	$k\ (265^{o}K) \times 10^{14}$ $cm^3\ molecule^{-1}\ sec^{-1}$	Lifetime Yrs $[OH]=2\times10^5$ molecule cm^{-3}	Lifetime Yrs $[OH]=6\times10^5$ molecule cm^{-3}
CH_3Cl	2.6	6.1	2.0
CH_2Cl_2	9.0	1.8	0.6
$CHCl_3$	7.3	2.2	0.7
C_2H_5Cl	26.3	0.6	0.2
CH_2ClCH_2Cl	12.5	1.3	0.4
CH_3CCl_3	1.2	13.2	4.4

SECTION 6

KINETICS OF THE HOMOGENEOUS GAS PHASE HYDROLYSIS OF CCl_3COCl, $CHCl_2COCl$, $CH_2ClCOCl$ and $COCl_2$

INTRODUCTION

When this study was initiated there were no kinetic data in the literature on the homogeneous gas phase hydrolysis of the three chloroacetyl chlorides. Data were available for the liquid phase hydrolysis of CH_3COCl[40] in 25% H_2O + 75% acetone mixtures which indicated that this reaction was quite fast. A pseudo first order rate constant of $k_{25^oC} = 8.6 \times 10^{-1}$ sec^{-1} was reported. The homogeneous gas phase hydrolysis of phosgene has been reported in the temperature range 220-420°C.[41] At 300°C, k = 10 liter $mole^{-1}$ min^{-1}, with an activation energy of 12.02 kcal $mole^{-1}$. The data were obtained in a high temperature infrared cell, but no error limits were given.

An experimental program was therefore undertaken to obtain homogeneous gas phase hydrolysis data for the four acid chlorides. Initially, it was thought that this would be a relaively simple task, but as experience showed, this was not to be the case for a variety of reasons. A brief resume of the early unsuccessful studies will be presented, followed by a more detailed account of the final experimental determination.

PRELIMINARY STUDIES - STATIC REACTOR

Initially an attempt was made to study the hydrolysis reactions in a static gas phase infrared cell and use IR to monitor the reactant and product concentrations. A few crude experiments were tried with a commercially available gas

cell. The initial results seemed encouraging though there were obvious indications that the acetyl-chlorides were attacking the buna-N, O-rings in the cell.

A static IR gas cell reactor and suitable thermostated enclosure were built. The latter was capable of temperatures up to $\sim 200^{\circ}C$. The gas cell is shown in Figure 12 and was constructed with the idea of minimizing possible attack by the acetyl chlorides on the cell materials.

Preliminary tests showed that the acetyl chlorides were attacking the Viton O-rings and the greased stopcocks. Several different O-ring materials were tried without success. Although Teflon O-rings would have been unreactive towards the acid chlorides they were not tried since it was thought they would not provide good sealing characteristics between the pyrex cell body and the relatively soft AgCl windows. To eliminate this problem the O-rings were removed and the window - pyrex seal made using glyptal wax. The grease lubricated glass stopcocks were replaced by all glass - teflon valves. With these modifications the acetyl chlorides could be maintained in the cell indefinitely.

Experiments were tried on the H_2O (g) + CCl_2H COCl (g) reaction. Initially experiments were made at $25^{\circ}C$ for periods of about 90 minutes with reactant concentrations being measured. The reaction appeared to be proceeding at a convenient rate, however, it was not possible to fit the data to any simple rate equation. Experiments were tried at $65^{\circ}C$ and $125^{\circ}C$ and it was found that the reaction rate actually decreased with temperature. This behavior strongly suggested that heterogeneous surface reactions were complicating the situation. This conclusion was further substantiated when glass beads were added to the reactor to deliberately increase the surface area and the reaction rate was found to increase almost in direct proportion to the added surface area.

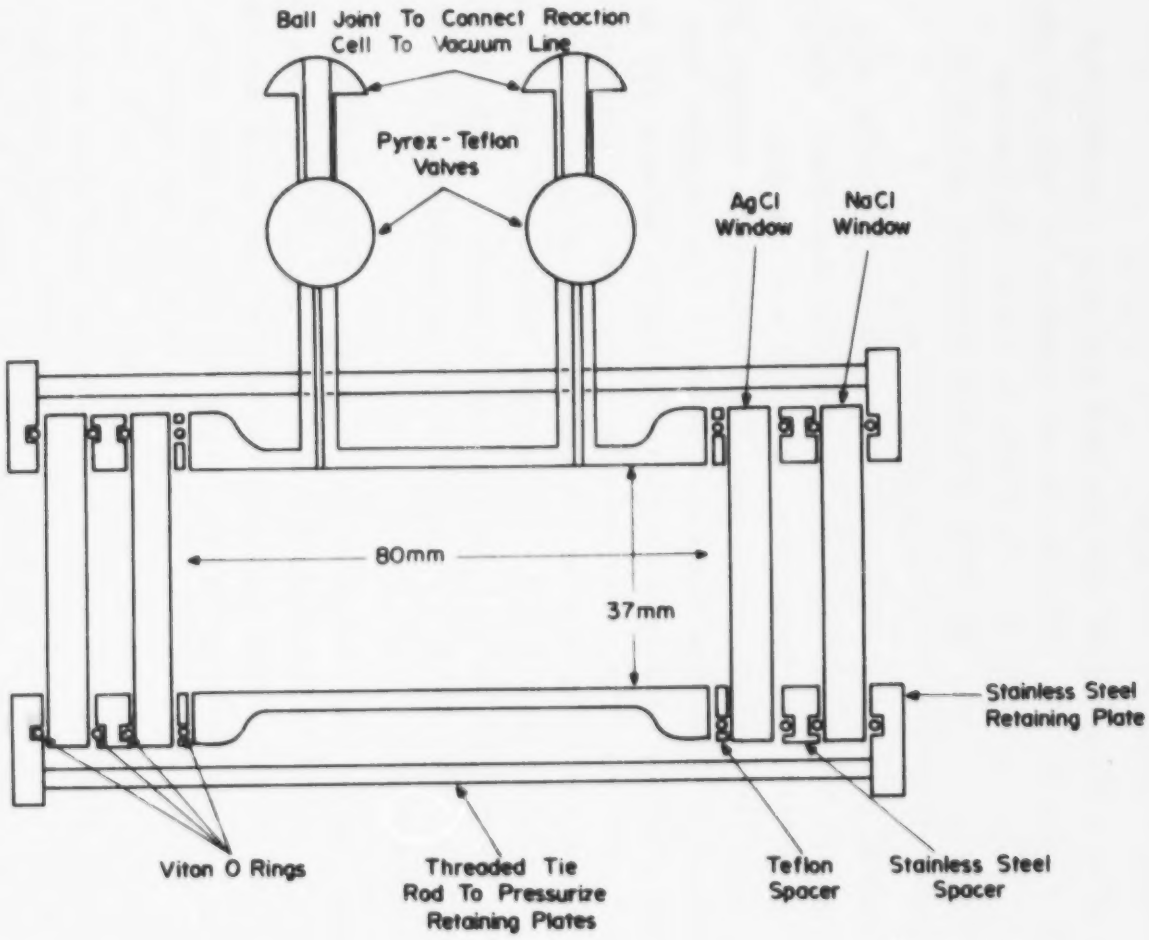

Figure 12. Static Infrared Reaction Cell to Study the Gas Phase Hydrolyses of $COCl_2$ and $CCl_nH_{3-n}COCl$ (n = 1, 2 or 3)

From these studies it was possible to conclude that the homogeneous gas phase hydrolysis of CCl_2HCOCl at ambient temperature was slow, $k \leq 0.06$ liter mole^{-1} sec^{-1} and could not be measured in the static IR cell. It was further noted that if the homogeneous gas phase hydrolysis rate for CCl_2HCOCl was of the same order as that of $COCl_2$,[41] a value of $k \simeq 10^{-5}$ liter mole^{-1} sec^{-1} could be expected at ambient temperature.

PRELIMINARY STUDIES - DYNAMIC REACTOR

Because of the above difficulties, a dynamic flow reactor system was built in which reaction temperatures up to 500°C and residence times of up to 20-45 minutes were attainable. The system is shown schematically in Figure 13.

Nitrogen was used as the carrier gas rather than air to avoid possible oxidation reactions with the acid chlorides at the elevated reaction temperature. Two independent N_2 carrier gas flow systems were used to obtain gas streams containing water vapor and the acid chloride vapors. To obtain a given gaseous concentration of the reactants, the carrier gas was passed through two thermostated bubblers (temperatures good to $\pm$ 0.1°C) containing either the acid chlorides or water. The two gas streams, saturated with the reactants at a given bubbler temperature could either be passed directly into the IR cell (this was the same cell used in the static measurements) to monitor the initial reactant concentrations or through the pyrex reactor and then into the IR cell to monitor the reactant concentration after the reaction. The gases from the IR cell were passed through a wet test meter so that the total gas flow through the reactor, and hence contact time in the reactor, could be determined. All valves in the system exposed to the acyl halides were of glass-teflon construction. Where necessary the carrier gas reactant lines were heated.

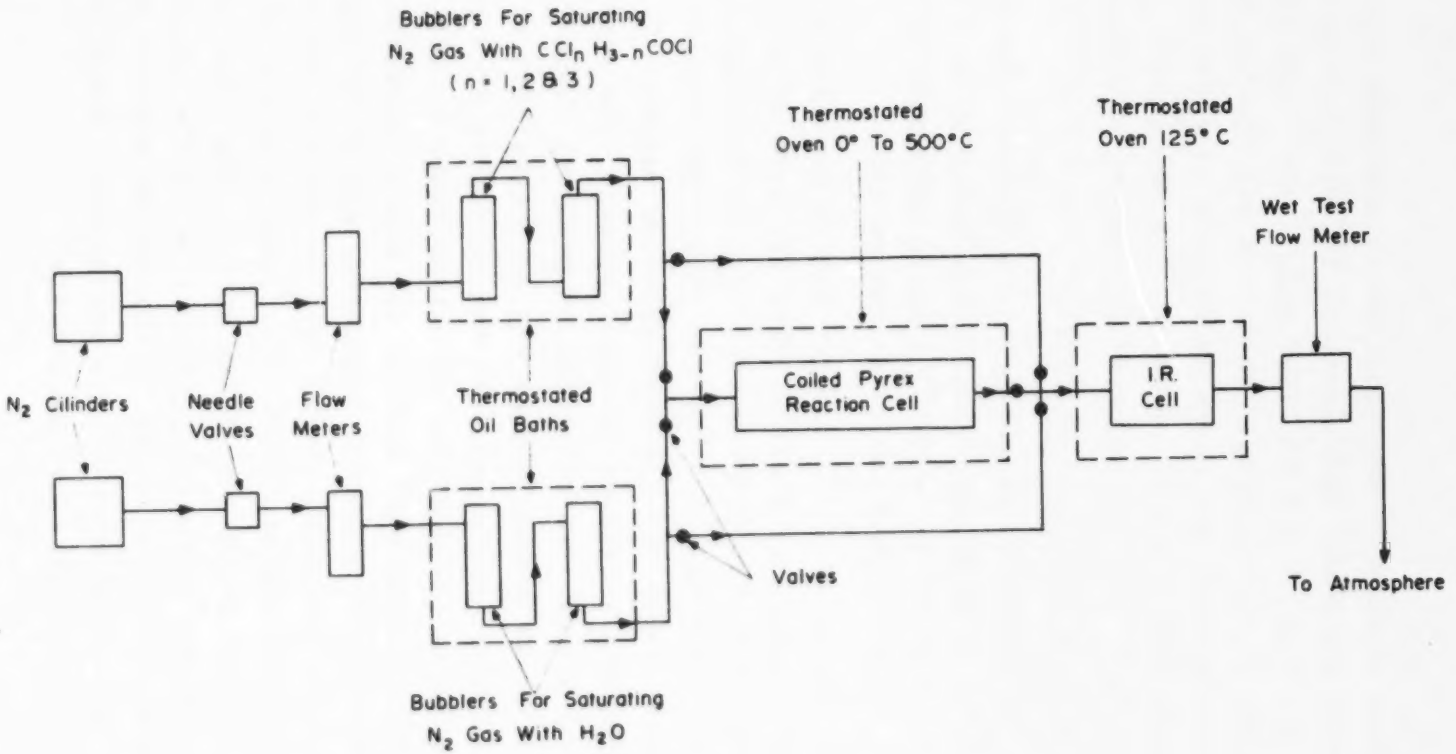

Figure 13. Dynamic Reactor System to Study the Gas Phase Hydrolyses of $COCl_2$ and $CCl_nH_{3-n}COCl$ (n = 1, 2 or 3)

The reactor initially had a volume of about 600 cc, though later this was increased to 3000 cc, and was of 18 mm ID pyrex tubing wrapped in a spiral with a diameter of about 6". The thermostated oven was capable of temperatures up to 500°C and could be controlled to $\pm$ 0.5°C. The IR cell was thermostated at 125 $\pm$ 0.25°C. Under the conditions used in these experiments, with a gas flow through the system of 30 to 500 cc minute, the amount of reaction occurring in the heated carrier gas reactant lines and within the IR cell was negligible compared to that occurring within the reactor proper.

The $COCl_{2(g)} + H_2O_{(g)}$ reaction was studied between 295 and 450°C in the reactor. The rate data appeared to be dependent on which reactant was in excess, and two temperature dependent equations for the rate constant were derived;

For excess H_2O, $k = 101\ e^{\frac{-8120}{RT}}$ liter $mole^{-1}$ sec^{-1} and

For excess $COCl_2$, $k = 19.8\ e^{\frac{-7030}{RT}}$ liter $mole^{-1}$ sec^{-1}

Next, the reaction $CCl_2HCOCl_{(g)} + H_2O_{(g)}$ was investigated between 215-325°C. The temperature dependent equation was as follows:

$$k = 24.3\ e^{(\frac{-5600}{RT})} \text{ liter } mole^{-1} \text{ } sec^{-1}$$

Some preliminary investigations were also made with $CClH_2COCl + H_2O$ and $CCl_3COCl + H_2O$, and the initial results indicated similar behavior as in the $CCl_2HCOCl + H_2O$ system. At this point experimentation was stopped for the following reasons.

Data precision was not good. This was due to at least to two problems. The full temperature range of the reactor could not be used due to decomposition of the acetyl chlorides at

elevated temperature as evidenced by carbon deposits on the walls of the reactor. All of these compounds started to decompose in the 290-325°C temperature range. This limitation on the usable temperature range necessitated extending the contact time by reducing flow rates, and difficulty was experienced in controlling and measuring these rates accurately. In the two systems studied in detail, $COCl_2$ and $CH_2ClCOCl$, the pre-exponential factors were $\leq$100 liter $mole^{-1}$ sec^{-1}, values much lower than would be expected theoretically. In addition, the activation energies also appeared to be too low. Both these factors could be caused by surface effects becoming more important at the lower reaction temperatures. Indeed, the volume: surface area of ratio of the reactor was not very large. If surface reactions were present, the unfavorable volume surface area ratio would certainly tend to magnify such effects.

Because of the above difficulties, it was decided to revert to a static reactor system in which the volume to surface ratio was as large as possible within the bounds of convenience and to use gas chromatographic sampling for the chemical analysis of the reaction.

EXPERIMENTS WITH THE LARGE STATIC REACTOR

Experimental

The experimental apparatus used in the homogeneous vapor phase reactions of water vapor with the three chlorinated acetyl chlorides and phosgene is shown schematically in Figure 14. It consisted of the following. A five liter spherical all glass reactor equipped with one port for filling and evacuation of the reactor and a second port for gas sampling. The sampling port consisted of a glass capillary tube extending approximately to the center of the reactor. A Swagelok union, modified to house a rubber septum seal, was mounted on the sampling port to permit syringe removal of samples. The reactor assembly

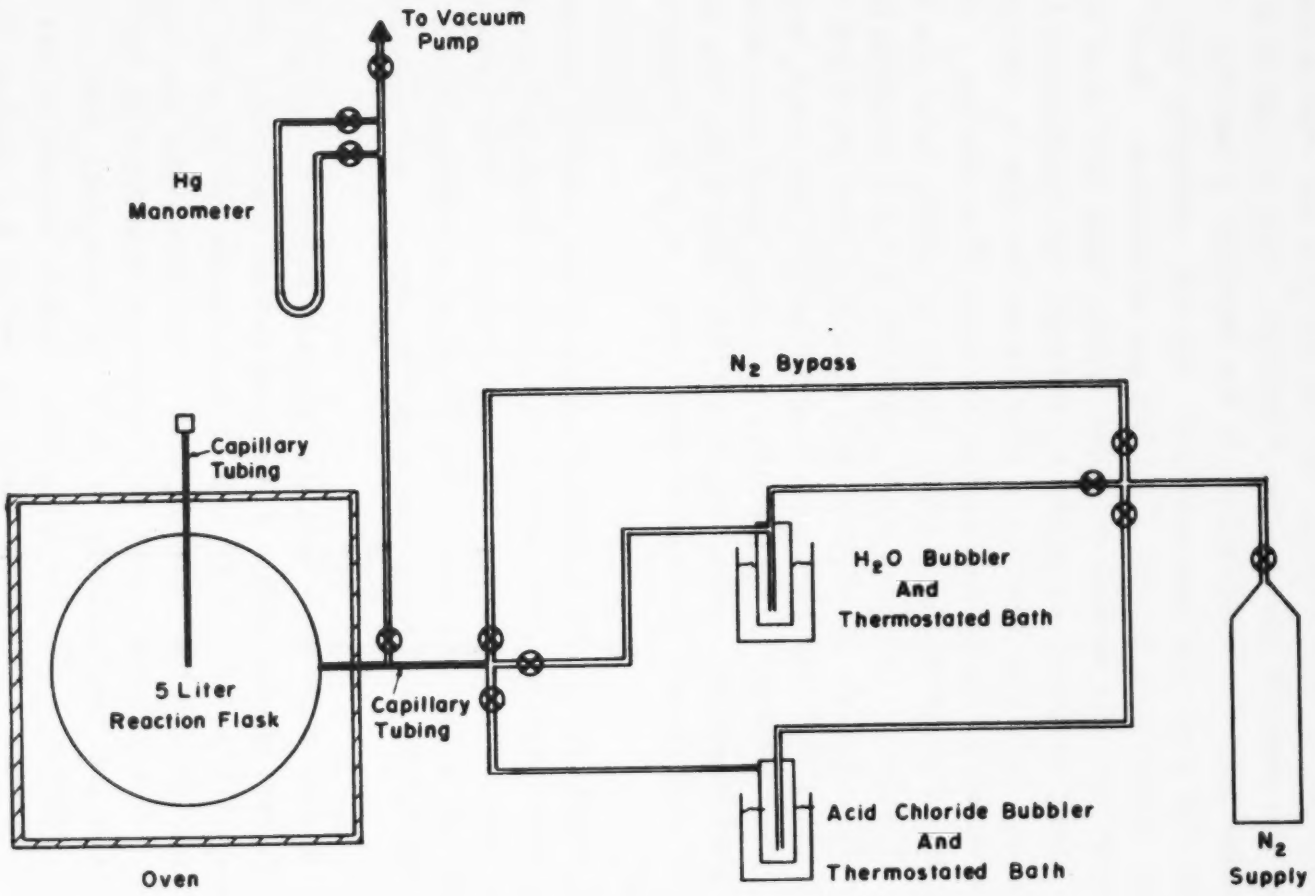

Figure 14. Schematic of the Reactor System Used to Study the Gas Phase Hydrolysis of the Chloroacetylchlorides

was mounted in a thermostated Labline oven, capable of operating up to a temperature of 350°C and stable to ±2°C.

Connected to the reactor via the filling and evacuation port was the reactor gas delivery system. This system consisted of a vacuum pump for evacuation of the reactor, a mercury manometer for pressure measurements, and two thermostated bubblers, controlled to ± 0.1°C, for gas saturation. Both water vapor and the acetyl chloride vapors were delivered by flowing Linde prepurified grade N_2 through the thermostated bubblers and into the reactor. Flow rates for the N_2 carrier gas were measured using calibrated Matheson flow meters. $COCl_2$ was delivered by bleeding a small amount of $COCl_2$ into the N_2 stream. The $COCl_2$ flow was also measured using a calibrated Matheson flow meter. $CClH_2COCl$ and CCl_3COCl were obtained from Eastman, CCl_2HCOCl was obtained from Fluka AG, and $COCl_2$ was obtained from Matheson. The acetyl chlorides were used without further purification. $COCl_2$ was liquified with a dry ice-acetone slush and "pumped on" to remove impurities. H_2O was laboratory distilled.

The reactor, at the selected temperature, was filled by removing the sampling port septum and flowing the reactant gases into the reactor and out via the sampling port. This process continued for about 1/2 hour. The flows were then stopped, the reactor sealed by replacing the sampling septum, and sampling begun.

The acetyl chlorides were quantitated using a Packard Model 427 gas chromatograph with a flame ionization detector. This was fitted with a 3 ft, 2 mm I.D. glass column packed with 10% SE-30 on Chromosorb WHP, 80/100 mesh. The flow rate was set at 30 ml/min. The injector port and detector were held at 150°C and the oven run isothermally at 80°C for $CClH_2COCl$ and CCl_2HCOCl, and at 100°C for CCl_3COCl. Sample injection was accomplished with a Precision Sampling Series A-2 syringe fitted

with a 12" "side port" needle. The long sampling needle was necessary in order to remove samples from the center of the reactor. Calibration of the gas chromatograph for the acetyl chlorides was accomplished by injecting gaseous samples of known volume and concentration. These calibration gases were prepared by saturating a slow flowing nitrogen gas stream through a liquid bubbler maintained at a known constant temperature (usually $0^{o}C$). Vapor pressure data were not available in the literature for any of the acetyl halides, and so these data were generated using standard vacuum line techniques. The resulting vapor pressure-temperature curves are shown in Figures 15, 16 and 17.

In the experiments involving $COCl_2$, direct monitoring of the phosgene was not made due to difficulties in reactant sampling and calibration of the chromatograph. For the $H_2O + COCl_2 \rightarrow CO_2 + 2HCl$ reaction, CO_2 was monitored instead on a Hewlett-Packard Model 5710A gas chromatograph with a thermal conductivity detector. This was used in conjunction with a 6 ft, 1/4" O.D. stainless steel column packed with Chromosorb 102, 80/100 mesh. The helium carrier gas flow rate was set at 40 ml/min; the injection port at $100^{o}C$; the detector at $200^{o}C$; the detector current at 200 mA, and the oven was run isothermally at $70^{o}C$. A premixed gas from Matheson containing 0.0498% CO_2 in air was used for calibration.

Initially H_2O was to be monitored using gas chromatography, but high humidity coupled with the tendency of H_2O to stick to the syringe wall made analysis difficult and time consuming. As an alternative, the efficiency of the H_2O bubbler in the gas delivery system was determined and the concentration of H_2O in the reactor was calculated from relative flow rates of the two reactant gas streams on filling. The bubbler efficiency was determined by careful use of the gas chromatograph.

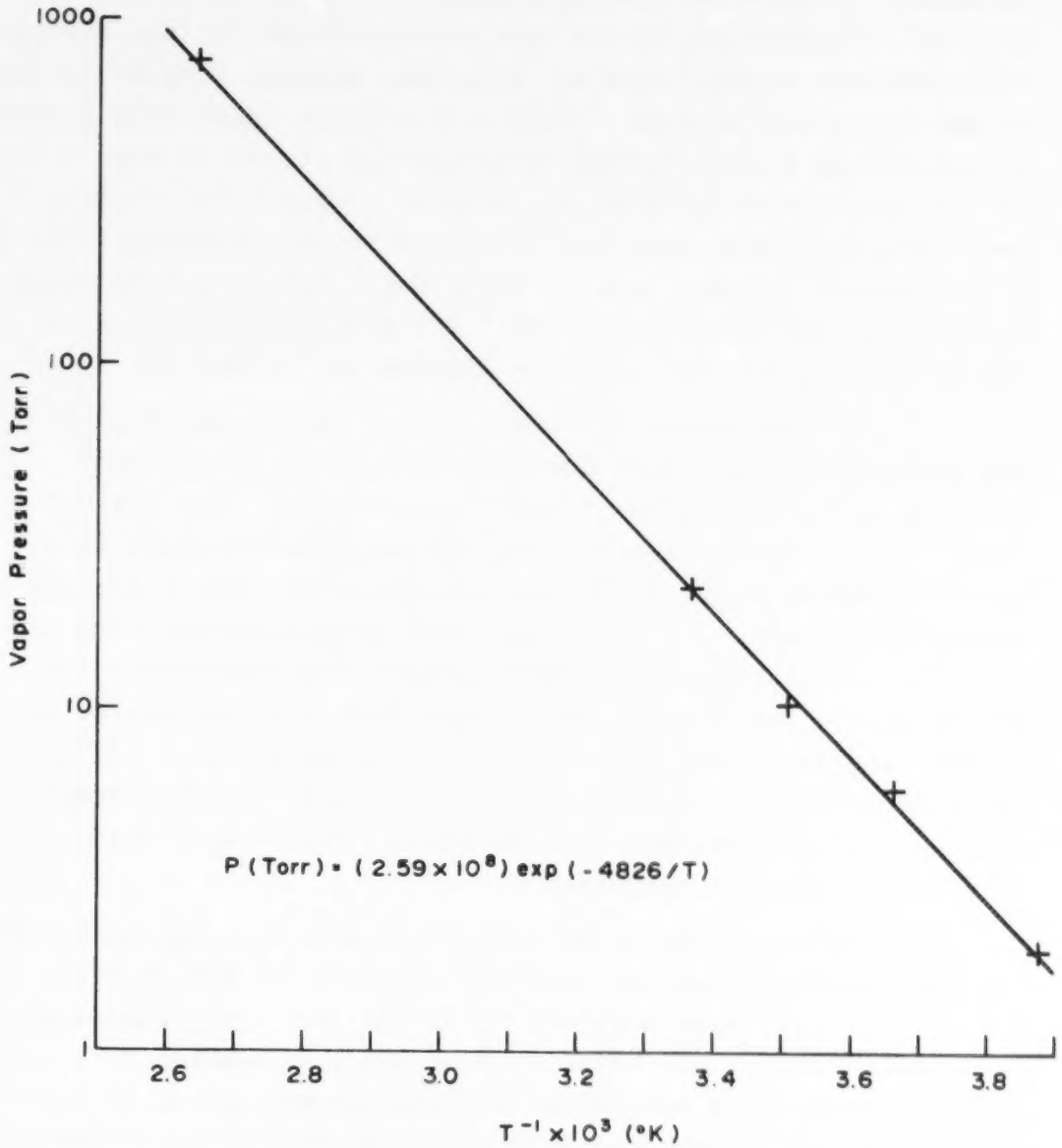

Figure 15. Vapor Pressure Curve for Chloroacetyl Chloride

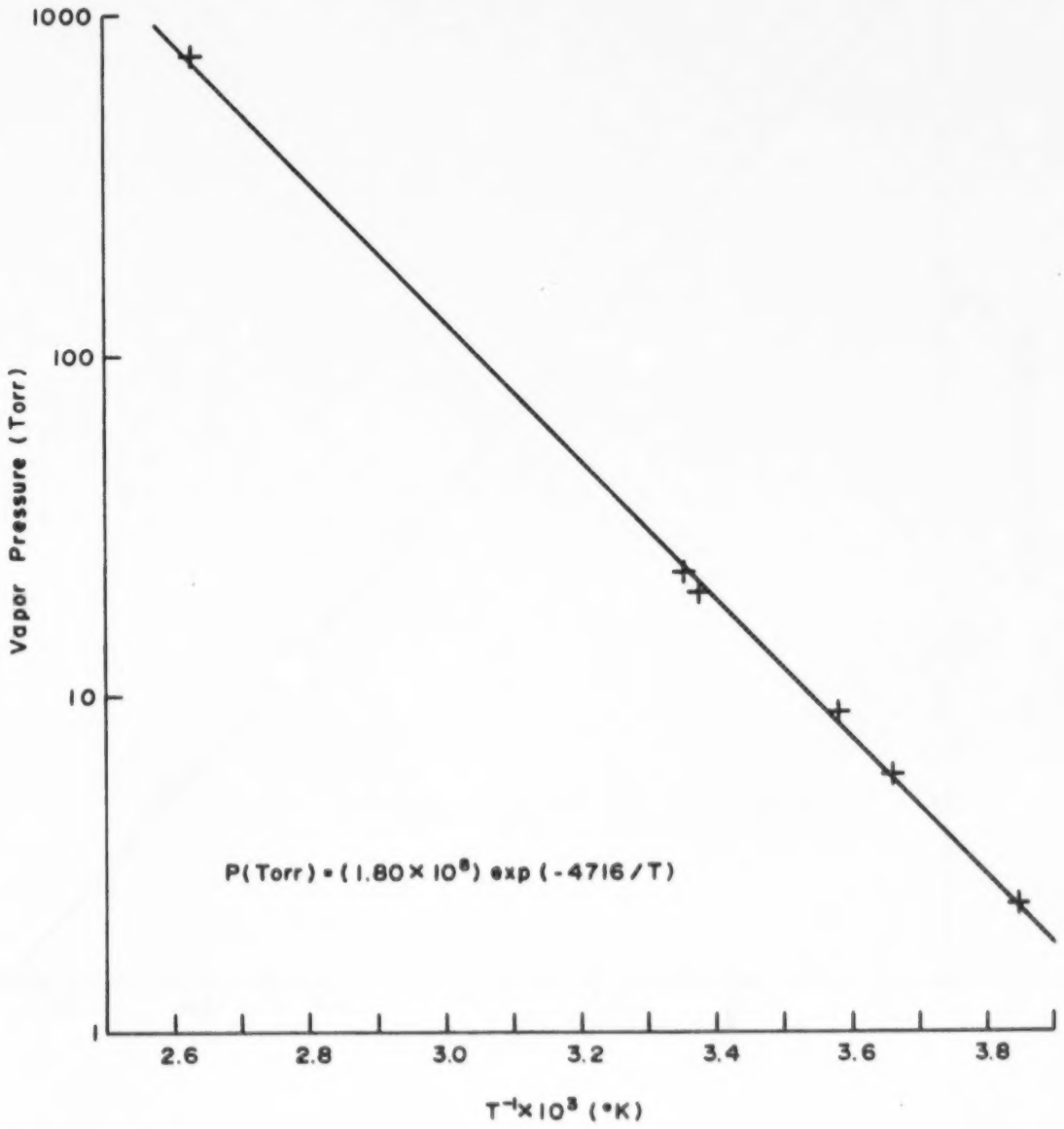

Figure 16. Vapor Pressure Curve for Dichloroacetyl Chloride

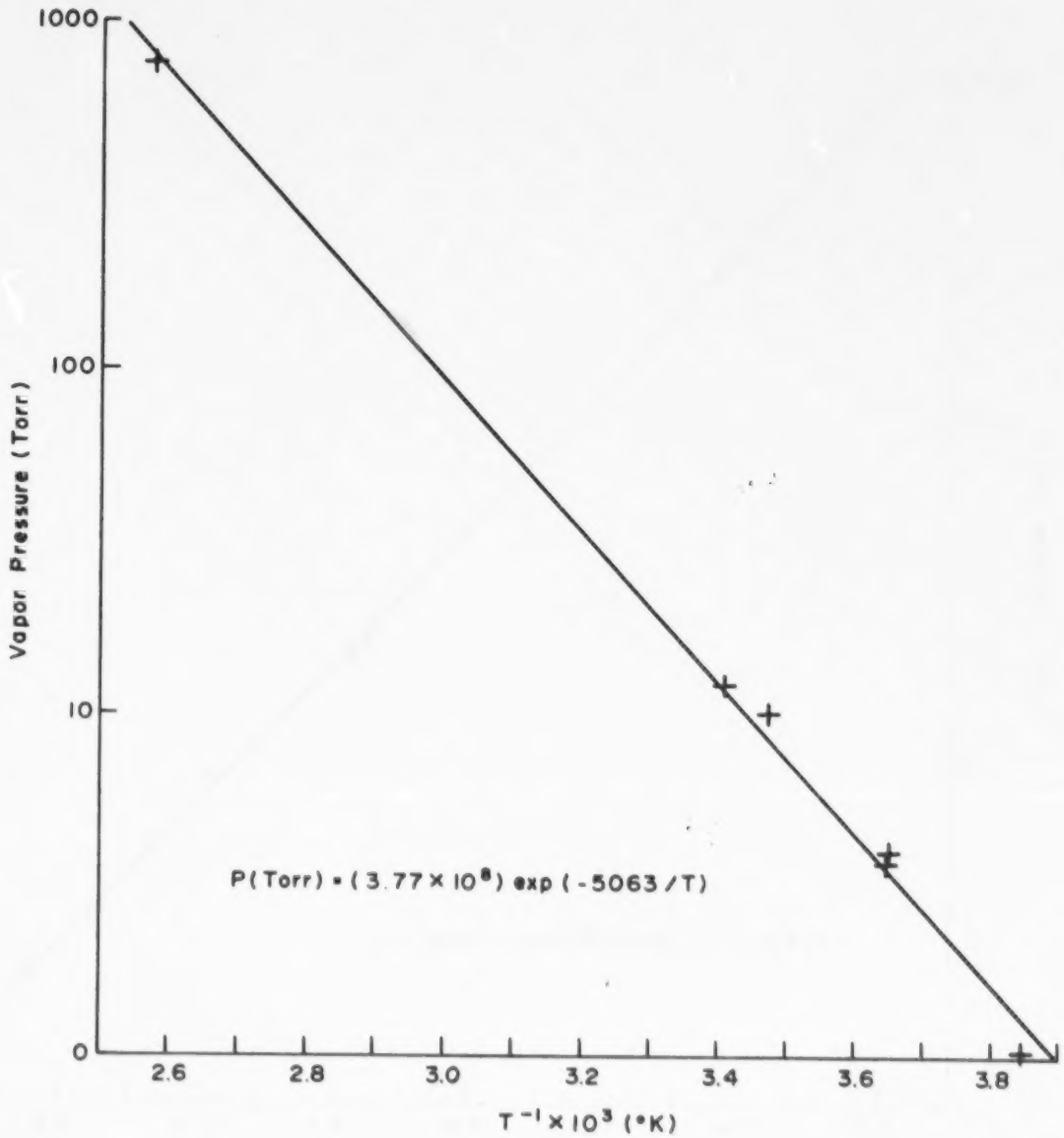

Figure 17. Vapor Pressure Curve for Trichloroacetyl Chloride

The same chromatograph using the same column and conditions as that described for CO_2, was used for H_2O analyses with the exception that the column was run isothermally at 100°C. The chromatograph was injected with several samples of N_2 saturated with H_2O, with each injection followed by several injections of N_2 alone. In this way, the immediate H_2O background of the syringe could be determined and the chromatograph was calibrated. Using the same procedure, samples of $N_2 + H_2O$ were taken from the gas delivery bubbler with the bubbler flow rate the same as that used in an experiment. From these data, the bubbler efficiency was calculated at 65%.

In a typical experiment when filling the reactor, the flow rate through the H_2O bubbler was set at 700 ml/min, and the flow through the acetyl chloride bubbler was set at 50 ml/min. In the $H_2O + COCl_2$ experiments, a $COCl_2$ flow of approximately 15 ml/min was bled into a N_2 stream of about 275 ml/min.

Depending on reaction rates, experiments usually lasted from 24 to 100 hrs with a sampling frequency of 20 to 60 minutes (nighttime excluded).

Results and Discussion

In order to interpret kinetically the data from the hydrolysis experiments on the acetyl chlorides and phosgene, the following three reactions were considered as possibly occurring;

$$A + B \rightarrow C + D \qquad k_1$$
$$A + B \leftarrow C + D \qquad k_2$$
$$A \rightarrow C + E \qquad k_3$$

where A = acetyl chloride or phosgene
B = H_2O
C = HCl
D = Chlorinated acetic acid for the acetyl halides and CO_2 for phosgene

E = unknown.

Reaction 1 represents the assumed bimolecular hydrolysis reaction. That this reaction is second order in reactants has been established for $COCl_2 + H_2O$ by the Russian workers.[41] For the acetyl halides, the reaction was simply assumed to be second order. Reaction 2, the reverse of reaction 1, was included since for the acetyl halides the experimental data indicated that an equilibrium was being established under the conditions being used. Finally, reaction 3 was included, since there was evidence for the mono and di-chloroacetyl chlorides, at the highest reaction temperature, that a small amount of thermal decomposition occurred to produce HCl and some unknown product. Similar thermal decomposition producing HCl did not occur for CCl_3COCl as would be expected, and indeed, in the temperature range studied, CCl_3COCl was stable. The following kinetic equations were derived to treat the experimental data.

Case I: Reaction #1 proceeding, A monitored, initial B measured.

$$\frac{-dA}{dt} = k_1 (A)(B)$$

	Concentrations			
	A	B	C	D
at time = 0	a	b	0	0
at time = t	x	(b-a+x)	(a-x)	(a-x)

$$\therefore \quad \frac{-dA}{dt} = k_1(x)(b-a+x)$$

$$k_1 = \frac{-dA/dt}{(x)(b-a+x)} \text{ at any time = t}$$

Case II: Reactions #1 and #2 proceeding, A monitored, initial B measured.

$$\frac{-dA}{dt} = k_1(A)(B) - k_2(C)(D)$$

	Concentrations			
	A	B	C	D
at time = 0	a	b	0	0
at time = t	x	(b-a+x)	(a-x)	(a-x)

$$\therefore \frac{-dA}{dt} = k_1(x)(b-a+x) - k_2(a-x)^2$$

Take several points along A vs t curve and obtain a best fit to $Z = Ax + By$

where: $Z = dA/dt$

$A = k_1$

$B = k_2$

$x = (x)(b-a+x)$

$y = -(a-x)^2$

Case III: Reactions #1, #2, and #3 proceeding, A monitored, initial B measured, k_3 known from separate experiment

$$\frac{-dA}{dt} = k_1(A)(B) - k_2(C)(D) + k_3(A)$$

	Concentrations				
	A	B	C	D	E
at time = 0	a	b	0	0	0
at time = t	x	(b-a+x+y)	(a-x)	(a-x-y)	y

$$\frac{-dA}{dt} = k_1(x)(b-a+x+y) - k_2(a-x)(a-x-y) + k_3(x)$$

$$y = \frac{dA/dt + k_1(x)(b-a+x) - k_2(a-x)^2 + k_3(x)}{-k_1(x) - k_2(a-x)}$$

Solve as for Case II using y = 0 at all points with the following Equation

$$\frac{-dA}{dt} - k_3(x) = k_1(x)(b-a+x+y) - k_2(a-x)(a-x-y)$$

Using the calculated k_1 and k_2, calculate all values for y and solve again. Repeat until k_1 and k_2 are obtained with desired precision.

In practice only Cases II and III were used for the water vapor plus acetyl chloride reactions. The existence of the reverse reaction (Reaction 2) was always considered to be a possibility. In those experiments where it was negligible, k_2 approximated to zero. Unfortunately, even when reaction 2 was significant it was not possible to calculate its value with good precision. In order to apply the above equations to the observed experimental data, reactant concentration versus time was plotted. A computer was used to obtain the best smooth line fit of the experimental data. A variety of mathematical forms were tried and an equation of the form $y = ae^{xb} + c$ was found satisfactory in all cases. Two typical hydrolysis-time curves are shown in Figures 18 and 19. The preceding equation was then used as a basis for calculation of the rate constants using the equations presented earlier. In Table 7 the experimental data are presented.

Only Case I was considered for the reaction of $COCl_2 + H_2O \rightarrow CO_2 + 2HCl$. The measured concentrations of CO_2 were plotted against time and fitted to the equation $y = ae^{bx} + c$. Since

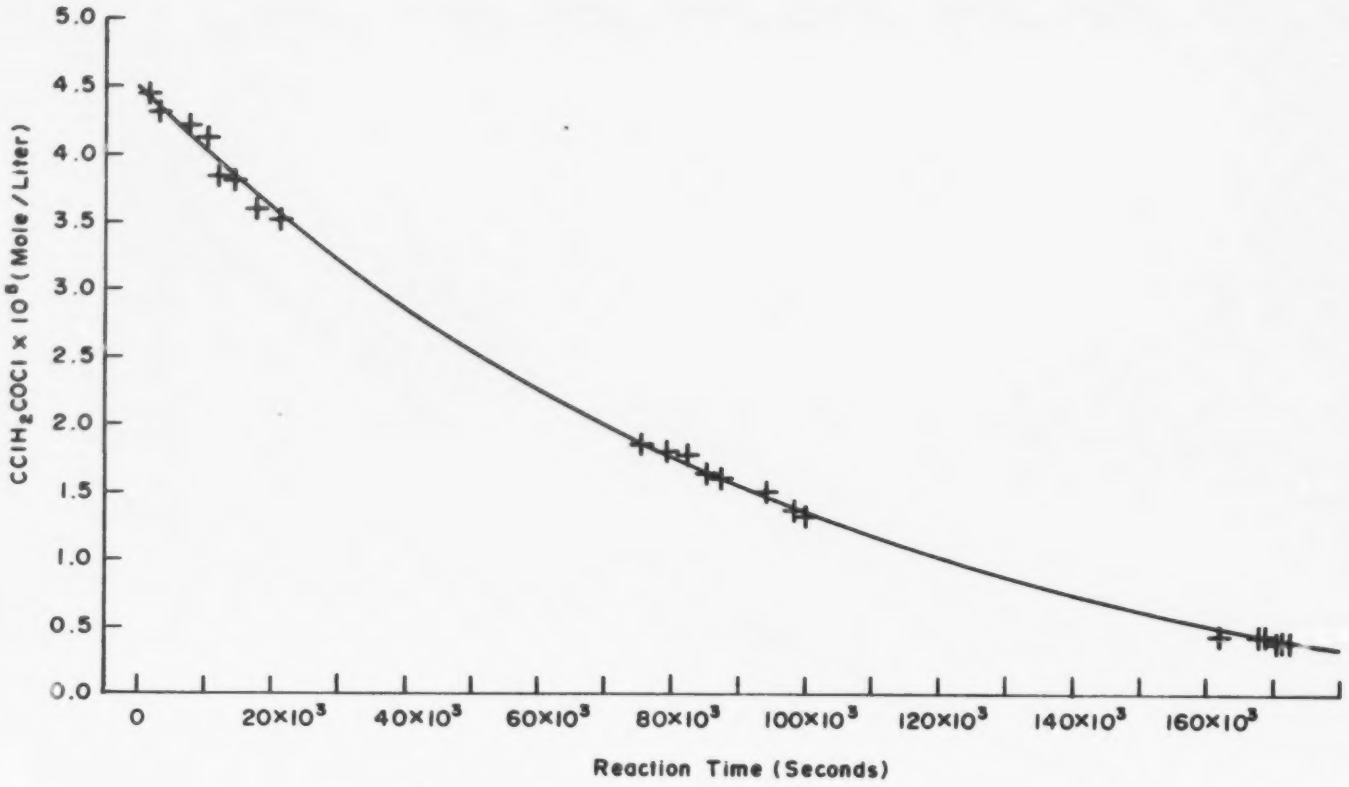

Figure 18. Experimental Data for the Homogeneous Gas Phase Hydrolysis of $CClH_2COCl + H_2O$ In N_2 at 517^oK

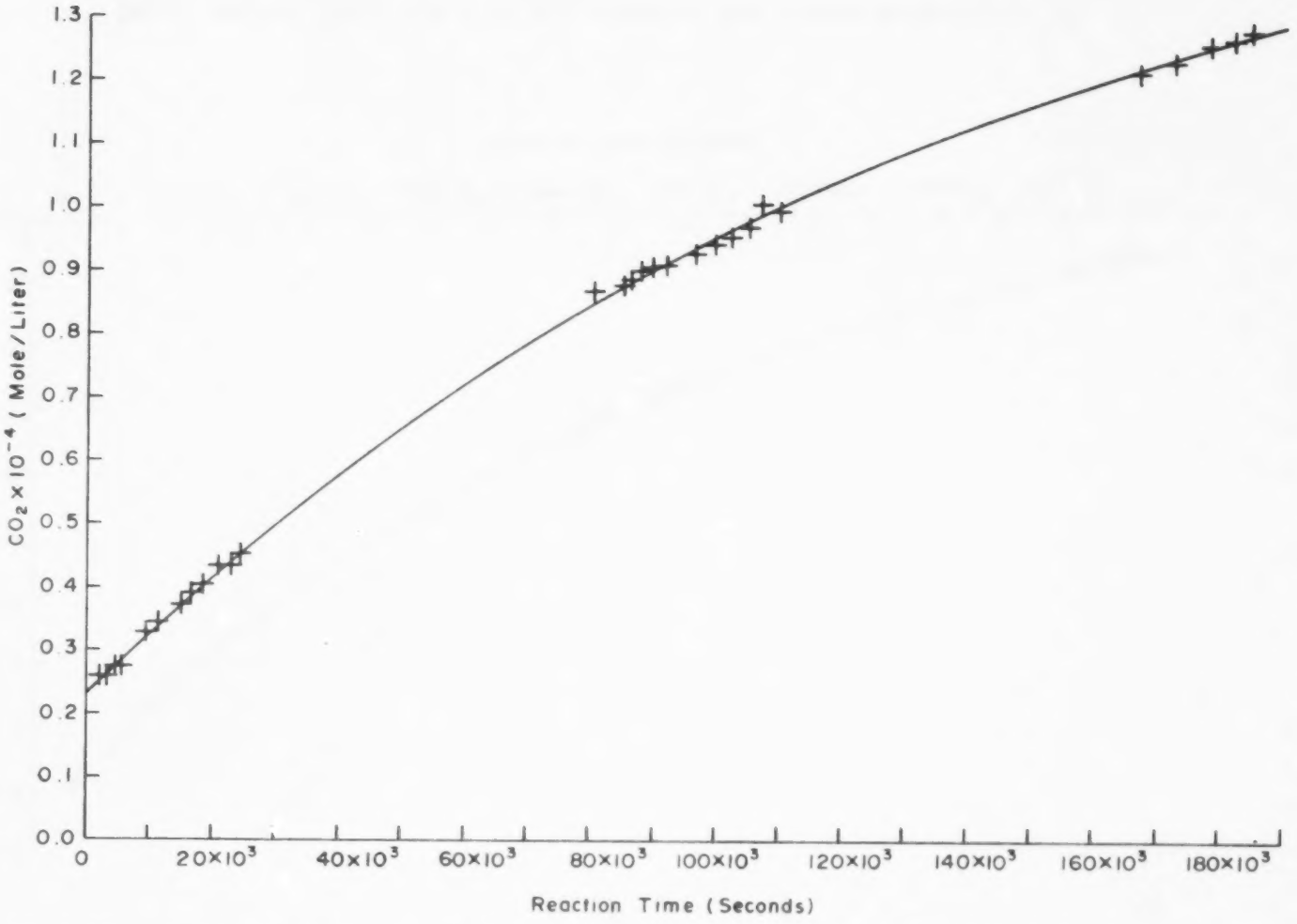

Figure 19. Experimental Data for the Homogeneous Gas Phase Hydrolysis of $COCl_2 + H_2O$ In N_2 at 544°K

Table 7

EXPERIMENTAL CONDITIONS AND RATE CONSTANTS FOR THE HYDROLYSIS EXPERIMENTS

$CClH_2COCl + H_2O$ in N_2

Expt.	Temp. (°K)	Initial $CClH_2COCl$ (mole-liter^{-1})	Initial H_2O (mole-liter^{-1})	k_1 (liter-mole^{-1}-sec^{-1})	Significant k_2?
1	533	1.45×10^{-5}	3.23×10^{-4}	0.0628	Yes
3	480	2.25×10^{-5}	3.75×10^{-4}	0.00578	No
6	508	2.10×10^{-5}	3.51×10^{-4}	0.0204	No
8	517	4.53×10^{-5}	3.71×10^{-4}	0.0292	Small
*5	530	2.52×10^{-5}	---	$K_3 = 3.45 \times 10^{-6}$ second^{-1}	

* This is A measurement of k_3 which was used in the calculation of k_1 in experiment 1. k_3 was insignificant at lower temperatures.

$CCl_3COCl + H_2O$ in N_2

Expt.	Temp. (°K)	Initial CCl_3COCl (mole-liter^{-1})	Initial H_2O (mole-liter^{-1})	k_1 (liter-mole^{-1}-sec^{-1})	Significant k_2?
19	473	5.41×10^{-5}	5.21×10^{-4}	0.00940	No
20	503	3.13×10^{-5}	4.33×10^{-4}	0.0264	Small
23	553	1.10×10^{-5}	3.82×10^{-4}	0.182	Yes
25	519	3.11×10^{-5}	4.14×10^{-4}	0.0436	Small
27	533	1.84×10^{-5}	4.32×10^{-4}	0.0611	Yes

k_3 was insignificant at the temperatures of these experiments

$COCl_2 + H_2O$ in N_2

Expt.	Temp. (°K)	Initial $COCl_2$ (mole-liter^{-1})	Initial H_2O (mole-liter^{-1})	k_1 (liter-mole^{-1}-sec^{-1})
31	561	2.17×10^{-4}	3.26×10^{-4}	0.0205
32	533	1.41×10^{-4}	3.70×10^{-4}	0.0153
33	580	2.60×10^{-4}	3.18×10^{-4}	0.0465
34	592	2.47×10^{-4}	2.99×10^{-4}	0.0460
37	611	1.98×10^{-4}	2.41×10^{-4}	0.0972
38	544	1.43×10^{-4}	2.70×10^{-4}	0.0260
39	592	1.77×10^{-4}	2.83×10^{-4}	0.0421
40	569	1.77×10^{-4}	3.26×10^{-4}	0.0241
41	619	1.59×10^{-4}	2.77×10^{-4}	0.108

H_2O was always in excess, the difference between the concentration of CO_2 at time = ∞ and time = 0 is equal to the initial concentration of $COCl_2$. Also, the production of CO_2 should exactly correspond to the reduction of $COCl_2$. This allowed k_1 to be calculated by monitoring CO_2 and by knowing the initial concentration of H_2O.

$CClH_2COCl$--

The $CClH_2COCl$ results are based on four experiments in the temperature range 480°C to 533°K. k_2 was significant only in the experiment at 533°K. Also at 533°K there was some thermal decomposition of $CClH_2COCl$ and this was measured by running an experiment with only $CClH_2COCl$ in the reactor and no H_2O. In this experiment, HCl was seen chromatographically as a probable product of the thermal decomposition. At 517°K thermal decomposition was insignificant and was ignored.

A qualitative experiment was performed in order to confirm the existence of the back reaction (2) at the higher temperature. N_2 was passed through a U-tube containing $CClH_2COOH$ and fed into the reactor together with HCl gas. The reactor oven was set at 528°C. $CClH_2COCl$ was found to be produced at a significant rate, thus verifying the existence of the back reaction. From the four experiments, the Arrhenius expression for the vapor phase reaction of $CClH_2COCl + H_2O$ was as follows:

$$k = (1.14 \times 10^8) \exp(-22{,}630 \pm 780/RT) \text{ liter-mole}^{-1}\text{-sec}^{-1}$$

The data points for the temperature dependence are shown in Figure 20.

CCl_2HCOCl--

Hydrolysis experiments for CCl_2HCOCl in the temperature range 476° to 546°K indicated that very little hydrolysis of the compound was occurring and that chemical equilibrium in the system must have been close to the starting conditions.

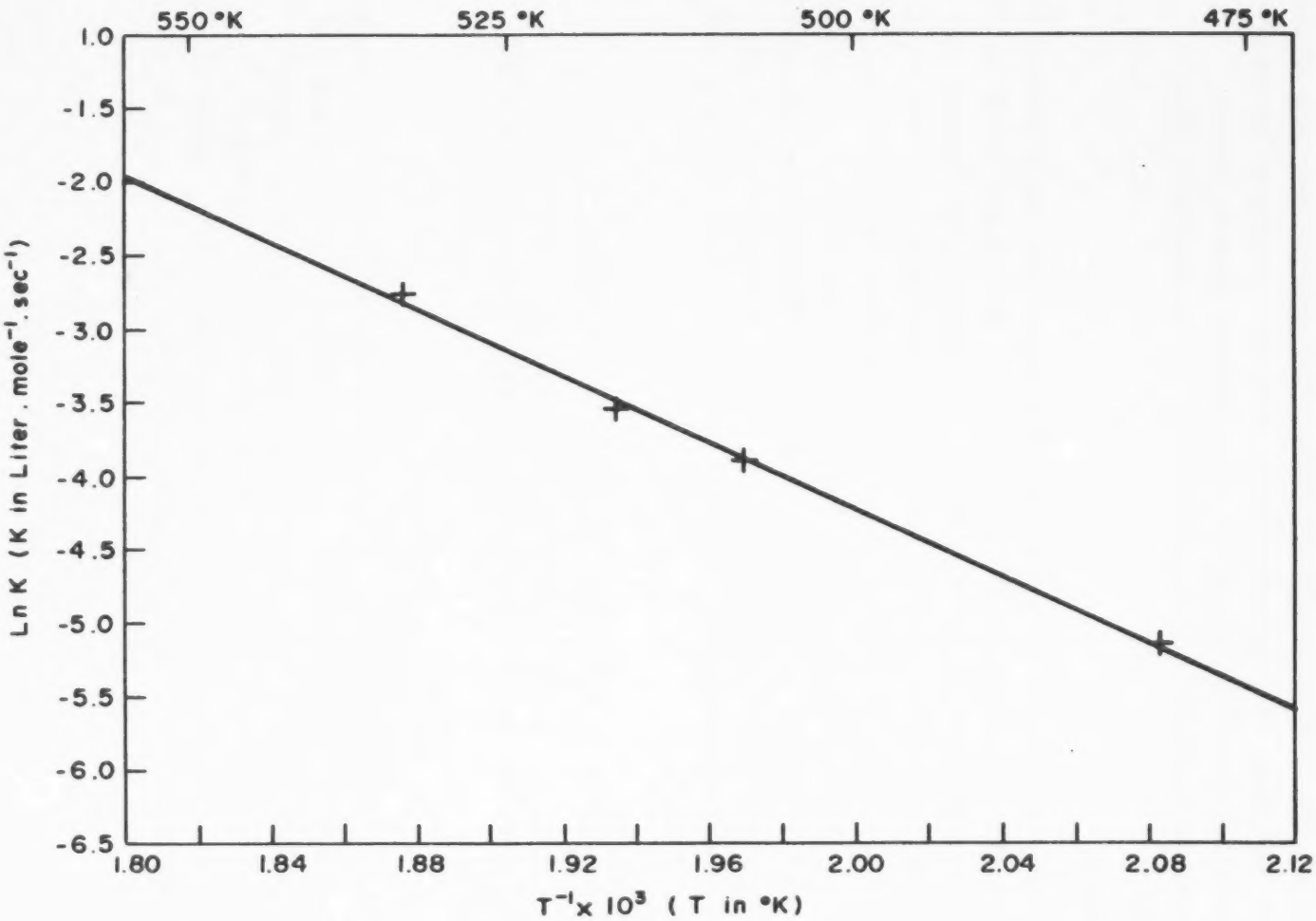

Figure 20. Arrhenius Plot for the Gas Phase Reaction $CClH_2COCl + H_2O$ In N_2 at a Total Pressure of 760 cm Hg

The latter in terms of reactant concentrations were similar to those used with $CClH_2COCl$. Because of the small extent of reaction, the experimental precision did not warrant any attempt to fit the data to a given kinetic scheme. Attempts to study the reaction outside the above temperature limits either resulted in reactant decomposition or on excessively slow reaction.

CCl_3COCl--

The results for CCl_3COCl are based on five experiments in the temperature range 437° to 553°K. k_2 was significant in the two experiments at 533°K and 553°C, and was insignificant in the lower temperature experiments. In all cases, k_2 was never important enough to have a significant effect on the value of k_1 (i.e., k_1 could be calculated using either Case I or Case II with little effect on the final answer). Thermal decomposition of CCl_3COCl was not significant in the temperature range of these experiments. The Arrhenius expression for $CCl_3COCl + H_2O$ is as follows:

$$k_1 = (2.54 \times 10^6) \exp(-18{,}350 \pm 1{,}750/RT)$$

The data points for the temperature dependence are shown in Figure 21.

$COCl_2$--

The results for $COCl_2 + H_2O$ are based on a total of 9 experiments in a temperature range of 533° to 619°K. These data were treated by the Case I equation, since thermodynamically,[42] the back reaction is known to be unimportant. Thermal decomposition was not important in the temperature range of the experiments. The Arrhenius expression for $COCl_2 + H_2O$ is as follows:

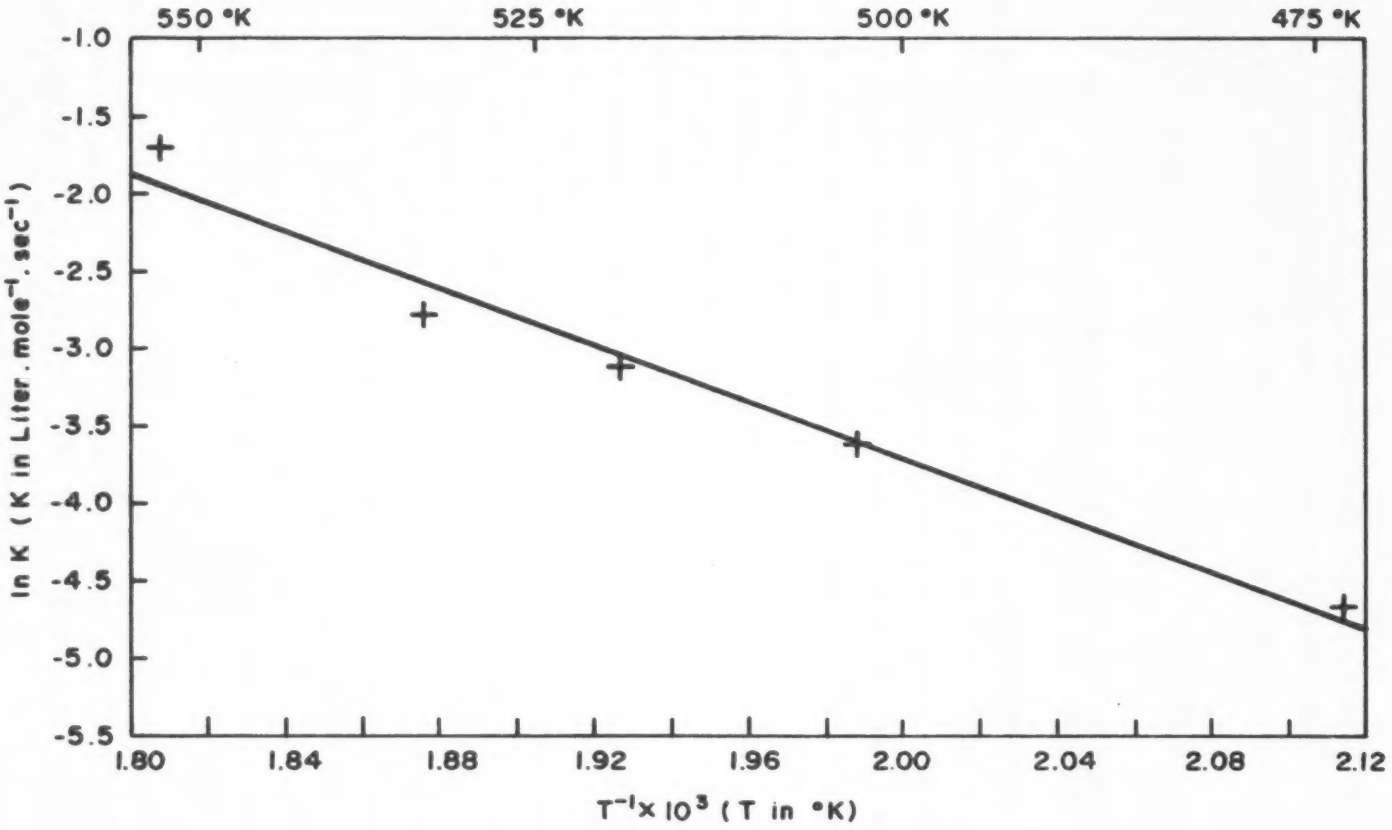

Figure 21. Arrhenius Plot for the Gas Phase Reaction $CCl_3COCl + H_2O$ In N_2 at a Total Pressure of 760 cm Hg

$$k_1 = (9192) \exp (-14{,}200 \pm 2100/RT) \text{ liter-mole}^{-1}\text{-sec}^{-1}$$

The data points for the temperature dependence are shown in Figure 22. The present result is in satisfactory agreement with the expression obtained by Gaisinovich and Ketov[41] of:

$$k_1 = (6250) \exp (-12{,}020/RT) \text{ liter-mole mole}^{-1}\text{-sec}^{-1}$$

IMPLICATIONS WITH RESPECT TO ATMOSPHERIC LIFETIME OF THE HOMOGENEOUS GAS PHASE HYDROLYSIS DATA

The primary object of the present study was to determine the tropospheric and stratospheric lifetimes of the acetyl chlorides and phosgene due to homogeneous gas phase hydrolysis. Using the usual formula[16] these lifetimes are tabulated for the assumed concentrations and temperatures in Table 8. Although there is a considerable uncertainty in the calculated lifetimes, a result of having to extrapolate values for the rate constants to considerably lower temperatures than that at which they were determined, there is no doubt that the lifetimes of these species due to homogeneous gas phase hydrolysis in the troposphere are indeed substantial and that unless other mechanisms are available for their removal there is no question that these species will all find their way into the stratosphere in large amounts. Kinetic data were not obtained for CCl_2HCOCl due to difficulties noted earlier but it is reasonable to assume that this compound will probably have a lifetime in the same range as the mono and trichloroacetyl chlorides. There is also no question that in the stratosphere, homogeneous gas phase hydrolysis will not occur except on a time scale which is absurdly large.

The present data leave no doubt that the homogeneous gas phase hydrolysis of these halides is not a viable sink for these compounds in the atmosphere. For this reason some preliminary

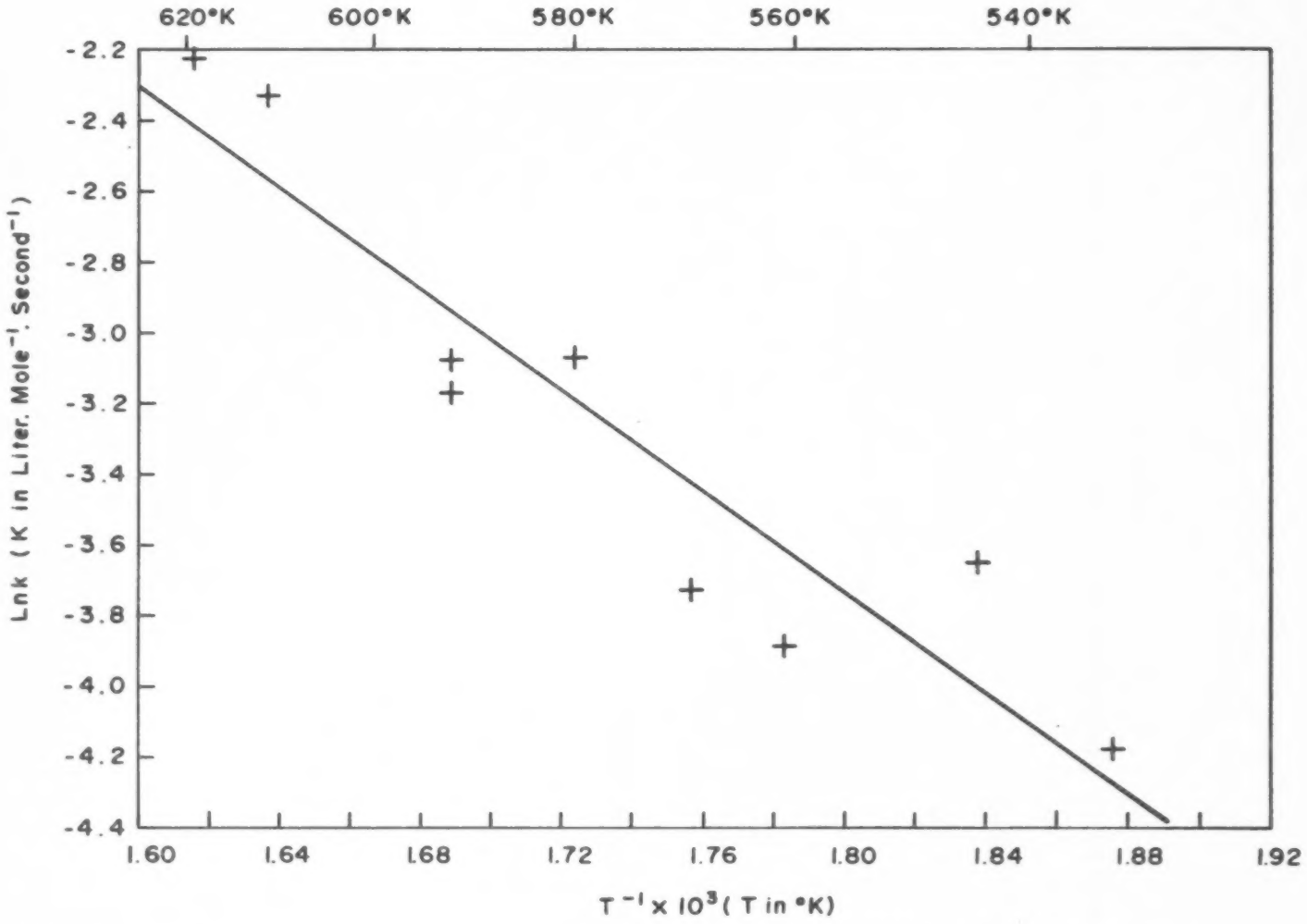

Figure 22. Arrhenius Plot for the Gas Phase Reaction $COCl_2 + H_2O$ In N_2 at a Total Pressure of 760 cm Hg

Table 8

CALCULATED ATMOSPHERIC LIFETIMES FOR CCl_3COCl, $CClH_2COCl$ AND $COCl_2$

At Sea Level

T = 298°K
Atm. P = 760 Torr
Acyl Chloride or Phosgene = 1 ppb (v)
H_2O Vapor = 10 Torr

$t_{1/2}$ $(CClH_2COCl)$ = 13,100 yrs. (range = 7,600 to 22,680 yrs.)
$t_{1/2}$ (CCl_3COCl) = 455 yrs. (range = 130 to 1595 yrs.)
$t_{1/2}$ $(COCl_2)$ = 113 yrs. (range = 20 to 630 yrs.)

In the Stratosphere

T = 220°K
Atm. P = 50 Torr
Acyl Chloride or Phosgene = 1 ppb (v)
H_2O Vapor = 1 ppm (v)

$t_{1/2}$ $(CClH_2COCl)$ = 1.4×10^{15} yrs. (5.0×10^{14} to 3.8×10^{15} yrs.)
$t_{1/2}$ (CCl_3COCl) = 4.0×10^{12} yrs. (4.0×10^{11} to 4.0×10^{13} yrs.)
$t_{1/2}$ $(COCl_2)$ = 8.2×10^{10} yrs. (4.2×10^{9} to 1.6×10^{12} yrs.)

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experimental studies were made on the heterogeneous hydrolysis or "rain-out" of these compounds in the atmosphere since this mode of removal could represent another possible sink for these compounds in the atmosphere. These experiments will be described in Section 7 of this report.

SECTION 7

KINETICS OF THE HETEROGENEOUS HYDROLYSIS OR "RAIN-OUT" OF THE ACID CHLORIDES

INTRODUCTION

In Section 6 of this report experimentation showed that the homogeneous gas phase hydrolysis rate of $CClH_2COCl$, CCl_2HCOCl, CCl_3COCl and $COCl_2$ to the acids in the atmosphere was not an effective removal process and that these species would have long atmospheric residence times as the acid chlorides and would certainly, if no other destruction process were present, find their way into the stratosphere and there add to the total chlorine burden.

It was therefore necessary to consider other mechanisms by which these compounds could be removed from the troposphere. One obvious possibility is the heterogeneous hydrolysis or "rain-out" of these species in the lower troposphere. There has been much effort spent on the problem of precipitation scavenging rates for trace gases in the atmosphere. The understanding of the problem is complicated by a number of factors including reversible sorption behavior, liquid phase mixing and chemical reaction. A rather thorough treatment of the problem has been given by Hales,[43] largely in terms of the macroscopic properties of the system, e.g., diffusion coefficients, functional solubility relationships, Henry's Law constant, individual mass transfer coefficients, overall mass transfer coefficients, properties of the liquid film-gas interface etc. Unfortunately application of the theory to specific cases is difficult because in general the physical properties required

to apply the theory are not available, hence its practical utilization is limited.

In view of the above difficulties, a somewhat different and simplified approach to the problem of rain-out has been taken based on the kinetic theory of gases. With this approach a single "wash out parameter" or effectively a sticking coefficient is determined experimentally as a function of a few experimental variables. Based on the experimental value of the sticking coefficient an estimate is made of the likely efficiency of the "rain out" process for the acetyl chloride removal.

THE SIMPLE RAIN-OUT MODEL

All the acetyl halides and phosgene undergo hydrolysis in contact with water. There have been several studies in the past on the rate of hydrolysis of phosgene.[44-46] In all of these, the phosgene was dissolved in water miscible organic solvents, water added, and the hydrolysis rate determined. Under the conditions of the experiments a 1st order rate constant at 25°C for phosgene hydrolysis was obtained,[44] $k = 1.3 \times 10^{-2}$ sec^{-1}. Data for the chloroacetyl chlorides are not available, but for acetyl chloride at 25°C a 1st order hydrolysis rate of 8.6×10^{-1} sec^{-1} was reported.[47] In the case of phosgene there was no evidence that the HCl formed in the hydrolysis reaction acted catalytically. There were indications that the reaction is base catalyzed.[48]

In terms of the present problem it is not obvious how these rate data can readily be used to determine rain out rates. The above rate data were determined under conditions different from those likely to be applicable to the gas phase - rain drop interaction occurring in the atmosphere.

In order, therefore, to make some meaningful estimate of rain out rates with a model amenable to simple experimental application the following approach was taken. It was assumed

that the rate of removal of the acetyl chlorides from the gas phase by contact with a rain drop will be proportional to the total number of collisions of the acid chloride molecules with the water droplet while the latter is traversing an atmosphere containing the acid chloride vapor. From gas kinetic theory, the following expressions may be derived easily:

$$\frac{d[\text{Acid}]}{dt} = k' \, N\left(\frac{kT}{2\pi m}\right)^{\frac{1}{2}} A$$

or

$$\Delta[\text{Acid}] = k' \, N\left(\frac{kT}{2\pi m}\right)^{\frac{1}{2}} A \, \Delta t$$

where

k' = effectively a sticking coefficient, i.e., the fraction of total collision between the acid chloride molecules and the water droplet surface which result in reaction

N = No. of acid chloride molecules cm^{-3}

k = Boltzmann's Constant 1.38×10^{-16} erg deg^{-1}

T = Absolute temperature

m = Mass of one molecule of acid chloride = $MW/6.0225 \times 10^{23}$

A = Surface area of one drop in cm^{-2}

Δt = Time in seconds for the drop to traverse the gas phase containing the acid chloride vapor

$\Delta[\text{Acid}]$ = No. molecules of hydrolyzed acid chloride (free acid) formed per drop of water in a time, Δt.

Kinetically the above model is equivalent to a 1st order reaction, with the rate of hydrolysis being independent of the water concentration. At the expected low concentration of these trace species in the atmosphere this would appear to be a

reasonable model. A further assumption of the model is that collisions resulting in hydrolysis also result in the hydrolyzed molecule remaining in the water droplet and not re-evaporating. At the expected low concentration of the acetyl chloride species in the atmosphere, and therefore low droplet concentration, Raoult's Law would predict very low vapor pressures for the dissolved acid. An experimental program was initiated to obtain values of k', the sticking or accommodation coefficient, for the organic acid chlorides.

EXPERIMENTAL

A schematic diagram of the simple experimental apparatus used to determine the sticking coefficients of the acid chlorides is shown in Figure 23. Droplets of distilled water were formed on a glass dropper (1 ml volumetric pipette in most experiments) at the rate of about 20-30 per minute. These droplets were allowed to fall through a known gaseous atmosphere and collected in suitable pyrex glass collector tubes. The collector tubes were cooled with liquid nitrogen to minimize splashing and keep the vapor pressure of the water essentially zero. Droplet size (assumed spherical) was determined by weighing a known number of droplets. With a given dropper, drop size appeared to be reproducible to $\leq \pm 1\%$.

A pyrex tube with a 25 mm ID was used to contain the known gaseous environment through which the droplets were allowed to fall. It had three sections joined by ball joints. A long central section ($\sim$160 cm in most experiments and $\sim$80 cm in a few expts.) and two shorter sections, one containing the liquid droplet former and the second the collector assembly.

Known gaseous atmospheres were introduced into the dropper column as shown in Figure 23. Gas streams A and B consisting of pure He (Linde Zero Grade) and in a few experiments Air (Linde Zero Grade) were metered into the column at known flow rates (stream A $\sim$ 240 cc/min and stream B $\sim$ 50 cc/min). The purpose

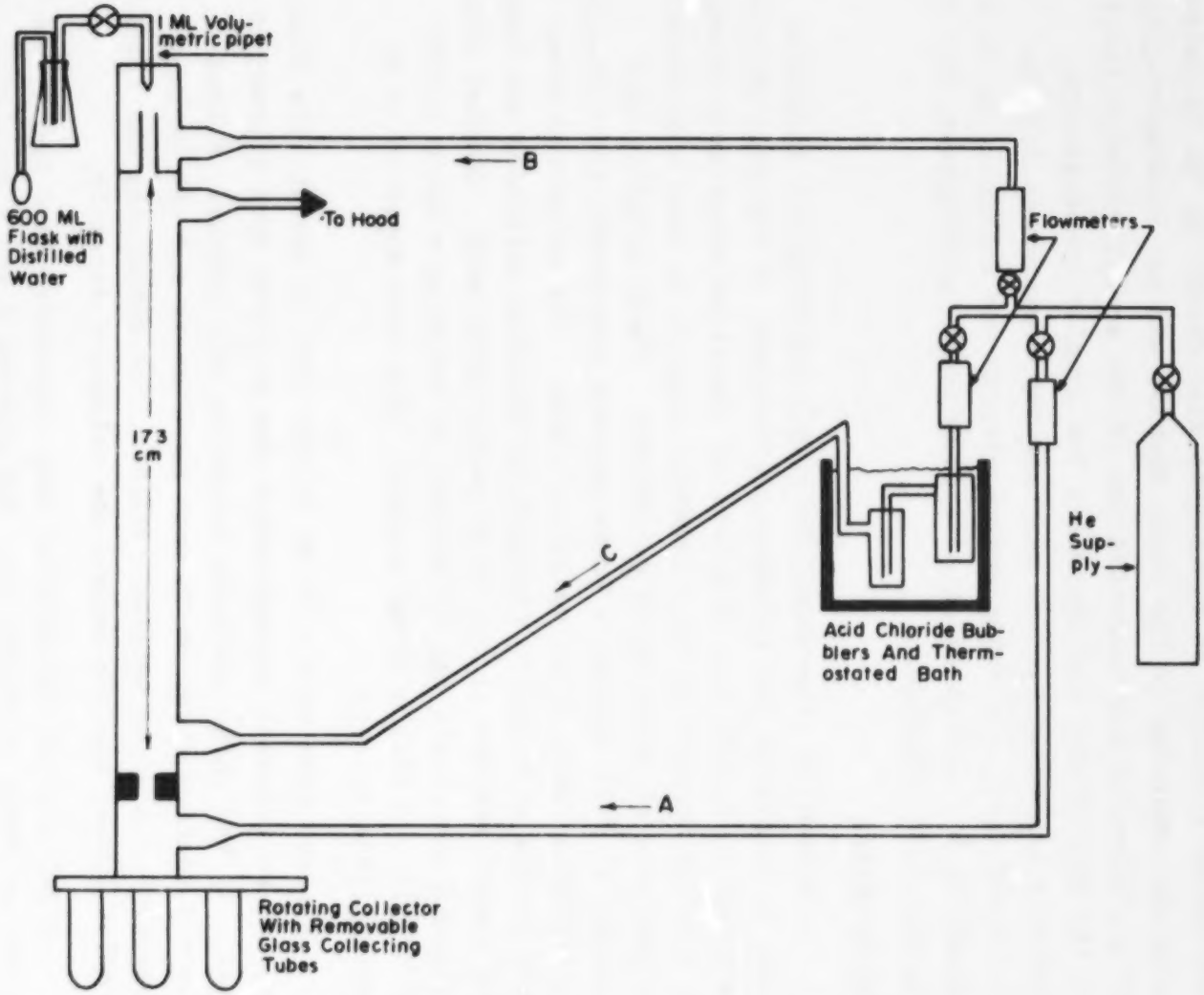

Figure 23. Schematic of the Acid Chlorides-Water Droplets Experiment

of these gas flows was to prevent diffusion of the acid chloride vapors into the collecting and droplet dispensing systems. Gas stream C contained the acid chloride vapor at a known pressure, generated by saturation bubblers in a thermostated bath. In most experiments the thermostated bath was held at $0^{o}C$, on a few occasions temperatures of $\simeq 20^{o}C$ was tried. Gas flows of $\simeq 200$ cc/min^{-1} were used. All three flow meters were calibrated against a wet test meter. The vapor pressure of the acid chloride in the dropper column was calculated from the known vapor pressure temperature curves presented in the previous section, and the relative gas flow rates. Prior to every set of experiments, careful tests were made to ensure that contamination of the droplet dispensing and the collecting systems with the acid chlorides was not occurring. Prior to collecting drops for analyses, the gas was set flowing through the system to allow equilibration and surface effects to be saturated.

Analysis of the water droplets for the acid chlorides was made chromatographically. Initially a Varian Model 1400 chromatograph equipped with a flame ionization detector was used. A 6 ft glass column packed with 80/100 mesh Chromosorb 101 was used to separate the water from the acids. This column had to be preconditioned prior to use by making several injections with pure water. Much difficulty was experienced with this unit and analytical precision was not very good. For this reason the analyses were finally made using a Hewlett Packard Model 5840A Gas Chromatograph fitted with a flame ionization detector and a 6 ft glass column packed with 60/80 mesh Carbopack B with 3% Carbowax 20M treated with 0.5% H_3PO_4. Due to lack of time this instrument was only used for analyses of CCl_3COOH, though it was suitable for all the chloroacids. It was necessary to precondition the column with water prior to use.

In Figure 24 a calibration curve is shown for CCl_3COOH which was made using solutions of known concentrations of the acid and

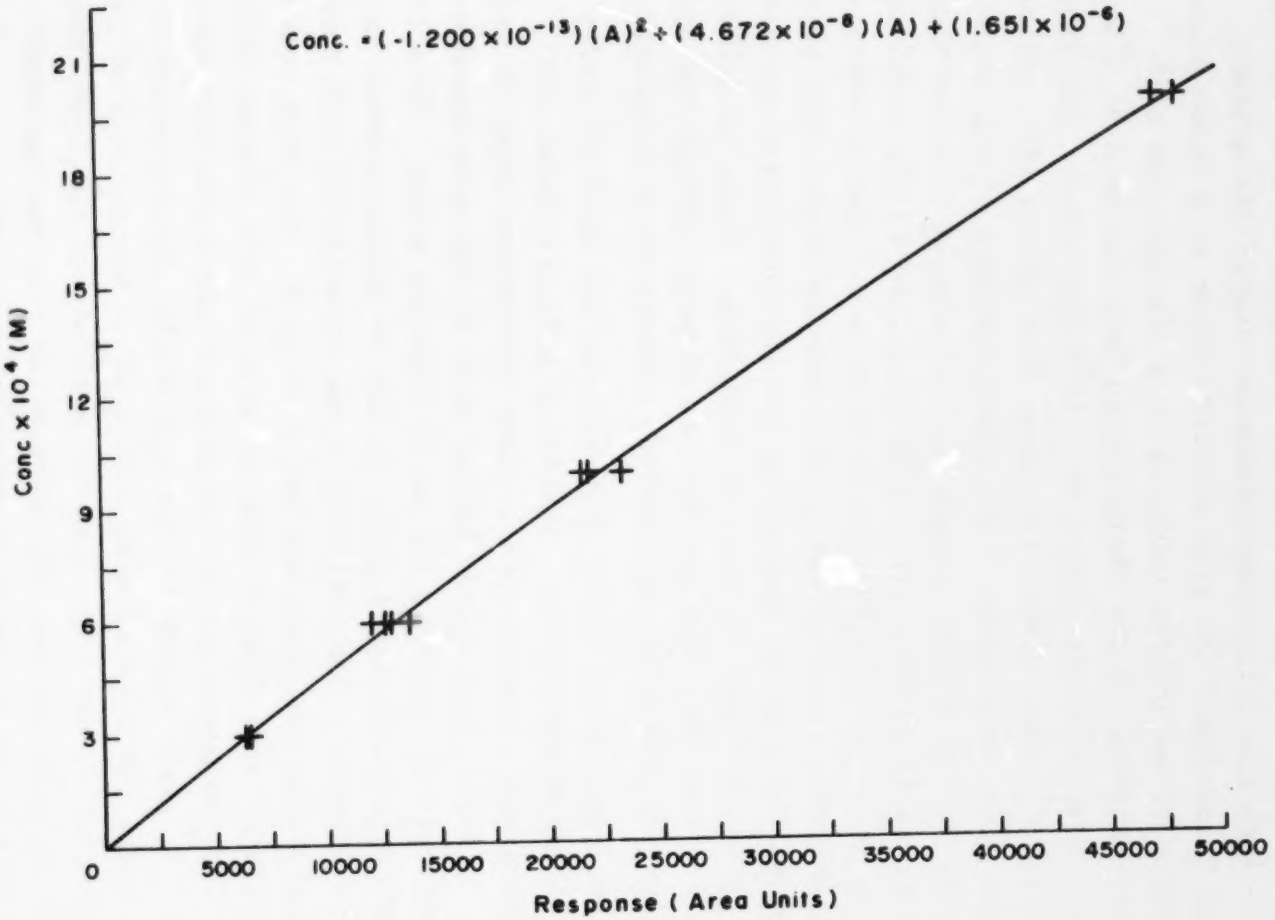

Figure 24. CCl_3COOH Calibration Curve

~1 μl injections. The acid was "Baker Analyzed" reagent grade. With this arrangement, the lower detection limit corresponds to an aqueous solution of 5×10^{-5} molar. In experiments, solution concentrations in the 1×10^{-3} to 5×10^{-4} M range were usually encountered.

Contact times of the drops in the column reactor were calculated based on the usual measuration formula. No attempt was made to account for gas viscosity or change in droplet shape. Because of the relatively short drop length employed, terminal velocity of the drop was not approached. (The radius of the drops used in the present investigation was of the order of 0.2 cm. These would have an atmosphere terminal velocity of about 900 cm sec^{-1}.[49] This compares with the value calculated for the longer drop experiments of ~580 cm sec^{-1}.)

RESULTS AND DISCUSSION

Lack of time, partly due to difficulties in developing a good analytical technique for the dissolved acid chlorides and also due to instrumental problems, prevented a detailed study of the "rain-out" kinetics of these species from being made. A summary of the data obtained is presented in Table 9.

The first three sets of experimental data on the mono, di and trichloroacetyl chlorides (Expts. 1, 2, and 3) were obtained using the Varian chromatograph for analyses of the dissolved acids. The accuracy of these data is uncertain. The results shown are the simple averages of two separate determinations on each of the acid chlorides. Due to chromatographic difficulties it is possible that these results could be in error by a factor of 5-10. Because of this, it is doubtful if much significance can be attached to the lower values of the sticking coefficient reported for the mono and di-chloroacetyl chlorides compared to the higher value for trichloroacetyl chloride.

Table 9

SUMMARY OF DATA OBTAINED IN THE RAIN-OUT EXPERIMENTS

Expt No.	Compound	Carrier Gas	Pmm Hg Acetyl Chloride	Ambient Temp. °C	Drop Surface Area (cm^2)	Contact Time (sec)	Sticking Coefficient k'
1	$CClH_2COCl$[a]	He	8.3	20	0.6729	0.6	2.82×10^{-4}
2	CCl_2HCOCl[a]	He	8.2	20	0.6729	0.6	2.23×10^{-4}
3	CCl_3COCl[a]	He	5.4	20	0.6729	0.6	8.07×10^{-4}
4	CCl_3COCl	He	5.4	20	0.6729	0.6	$6.69 \pm 0.17 \times 10^{-5}$
5	CCl_3COCl	He	2.1	20	0.6729	0.6	$1.10 \pm 0.03 \times 10^{-4}$
6	CCl_3COCl[b]	N_2	2.1	20	0.6729	0.6	8.27×10^{-5}
7	CCl_3COCl	Air	2.1	18	0.6729	0.6	$7.50 \pm 0.06 \times 10^{-5}$
8	CCl_3COCl[c]	He	2.1	20	0.6729	0.6	$7.85 \pm 0.06 \times 10^{-5}$
9	CCl_3COCl	He	2.1	20	0.4408	0.6	$1.38 \pm 0.23 \times 10^{-4}$
10	CCl_3COCl	He	2.1	20	0.4408	0.47	$9.92 \pm 0.90 \times 10^{-5}$

a) Results obtained with Varian chromatograph, all other data obtained with Hewlett Packard chromatograph.

b) Result from one experiment only.

c) Water droplets formed from an aqueous solution 2.68×10^{-4}M in CCl_3COOH

The remaining experiments shown in Table 9 (Expt. Nos. 4 through 10) were made using the Hewlett Packard gas chromatograph for the chlorinated acetic acid analyses. Because of lack of time, data were only obtained for trichloroacetyl chloride. However, the analytical procedure was reliable. Generally, three or four separate experimental determinations were made in deriving the values of the sticking coefficients presented in Table 9 and the errors there shown are the standard deviations of the separate experiments.

There is poor agreement between Expts. 3 and 4 shown in Table 9 which were run under identical conditions but with different chromatographic analyses as noted earlier. These results confirmed the previous suspicions on the unreliability of the earlier experiments. Before returning to Expt. 4, the results of Expts. 5 through 8 will be considered since these were all made with the same pressure of trichloroacetyl chloride in the vapor phase.

Expt. 5 will be used as a base from which to discuss the other results. Under the conditions of the experiment a sticking coefficient of $1.10 \pm 0.03 \times 10^{-4}$ was obtained. For a reactive system like the present one, the apparent observed sticking coefficient seems rather low. Part of the reason for this is probably due to diffusion limited gas transport to the drop. In the proposed simplified model this type of effort is not taken into account. It appears reasonable to support that the drop rapidly depletes a region of the gas phase around itself of the trichloroacetyl chloride, and that further pick-up by the drop of the reactive chloride is a time dependent diffusion controlled process.

If in fact the process is diffusion controlled then to some extent, depending on the importance of the diffusion process, the sticking coefficient obtained in air mixtures rather than helium mixtures should be smaller since rates of

diffusion of the acetyl chloride in air will be lower than in helium.[50] This is exactly the trend which is observed k'(air) = $7.5 \pm 0.06 \times 10^{-5}$ compared to k'(helium) = 1.10×10^{-4}. The relative rates of diffusion of the trichloroacetyl chloride in helium and air is not known, but a factor of at least 3 is probable.[50] The fact that the apparent sticking coefficient only decreases by about 25% in air compared to helium suggests that the diffusion limitations on the scavenging process are of some significance, though not of overriding importance. Diffusional processes are relatively slow compared to gas-surface collision processes. In the present experimental arrangement diffusion limited processes are over emphasized. The drop starts out with zero velocity and attains a maximum value of $\sim$580 cm second. This compares to the situation existing in the atmosphere where a drop of comparable size is travelling at its terminal velocity of $\sim$900 cm sec^{-1} for most of its lifetime.

Expt. 8 was run in essentially the same way as Expt. 5 except the water droplets were formed from an aqueous solution containing 2.683×10^{-4} M CCl_3COCl. This latter concentration corresponded to typical values found in the rain drops in Expt. 5. The sticking coefficient of $7.85 \pm 0.06 \times 10^{-5}$, Expt. 8, was lower than that when no chloroacetyl chloride was present initially. This result strongly suggests the sticking coefficient does depend on the concentration of the chloroacetyl chloride in the rain drop, at least at the concentration used in these experiments. In the atmosphere the chloroacetyl chlorides are present at very low concentrations, and rain drop concentrations will probably not attain such high values as used here. Consequently, this may not be a very important effect in the real life rain out situation. (As shown later, rain drop concentrations are probably $\leq 10^{-8}$ M in the chloroacetyl chloride.) The effect of high chloroacetyl chloride concentrations in the rain drop may be responsible for a low

sticking coefficient observed in Expt. 4 $k' = 6.69 \pm 17 \times 10^{-5}$ with P (acetyl chloride) = 5.4 mmHg (measured droplet average concentration $\sim 5 \times 10^{-4}$ M).

In Expt. 9 the drop size was reduced, the surface area being diminished to 0.4608 cm^2 from that of 0.6729 cm^2 used in the previous experiments. Within the error limits of the data $k' = 1.38 \pm 0.23 \times 10^{6}$ and $k' = 1.10 \pm 0.03 \times 10^{6}$ for the smaller and larger drop sizes, respectively, there is no significant difference in the sticking coefficients.

In Expt. 10 the contact time was reduced from 0.6 seconds used in all the previous experiments, to 0.47 seconds. The value of the sticking coefficient at $k' = 0.92 \pm 0.90 \times 10^{-5}$ is barely significantly different from that obtained with the longer contact time, of $1.38 \pm 0.23 \times 10^{-4}$. In view of a possible 10% error in the calculated contact times it would be premature to attach too much significance to this possible difference.

Finally, and not shown in Table 9, tests were made to determine if any significant loss of the dissolved acid was occurring during the drop period. Droplets 2.683×10^{-6} M in CCl_3COOH were allowed to drop through an atmosphere of pure helium with a contact time of 0.6 seconds. No discernible differences in acid concentrations before and after the experiment were found.

IMPLICATION OF "RAIN DROP" EXPERIMENTS WITH RESPECT TO ATMOSPHERIC WASH OUT OF THE ACID CHLORIDE

Although the above data from the "rain out" experiment must be regarded as somewhat tentative in nature, lack of time preventing an in-depth study of the phenomenon being made, it is instructive to make a preliminary estimate of atmospheric wash out rates for CCl_3COCl.

A value of 7.5×10^{-5} was obtained for the sticking coefficient of CCl_3COCl in air under the conditions of the experiment. Compared to the atmospheric situation, this value may be somewhat too low, due to the relatively high concentration of acid in the drop, and somewhat too large due to an over emphasis of a diffusional contribution to the observed sticking coefficient. In the absence of any data at this time to correct these effects, it will be assumed that they contribute equal but opposite effects, and that the value, $k' = 7.5 \times 10^{-5}$, for the sticking coefficient, is probably not too much in error for the proposed atmospheric application.

In order to make the wash out estimate the following conditions will be assumed:

CCl_3COCl mixing ratio = 0.1 ppb (v)

Rain drops only exist below an altitude of 5 km[51]

All the rain drops have a diameter of 2 mm

An average atmospheric pressure of 60 cmHg and temperature of 282°K

Rain drop terminal velocity of 900 cm sec^{-1}[49]

An average yearly rainfall of 100 g cm^{-2}.[52]

With the above assumptions, it is found that 1.16×10^{15} molecules cm^{-2} yr^{-1} of CCl_3COCl would be purged from the atmosphere. This quantity may be compared with the number of molecules of CCl_3COCl in a column of air 5 km high, at a concentration of 0.1 ppb (v), of 1.03×10^{15} molecules cm^{-2}. Thus a compound with a sticking coefficient of $\sim 7.5 \times 10^{5}$ has an atmospheric half life of about 5 months towards wash out by rain in the above simplified, though not unrealistic model. In the above calculation the temperature coefficient of the sticking coefficient has been ignored. If the temperature dependence of the process is similar to that of the heterogeneous hydrolysis of

CH_3COCl and $COCl_2$.[44] the above half life would probably be about 1 year.

These preliminary findings on the rain out rate for trichloroacetyl chloride give reason for concern for the following reasons:

Although the value obtained for the sticking coefficient of trichloroacetyl chloride must be regarded as a preliminary quantity it is difficult to imagine that it is in serious error. It would therefore seem that effective low values of sticking coefficient might be rather common for trace gas - rain droplet type interactions. The present value obtained for CCl_3COCl, could be in error by a factor of 2 to 3, which if in the wrong direction would result in a half life approaching 3 years. This would probably not result in a significant amount of CCl_3COCl entering the stratosphere. R. J. Ciceone, private communication, suggests that a half life of about 5 years could result in a significant quantity of a material like CCl_3COCl entering the stratosphere, but admits that atmospheric wash out phenomenon are not well understood. He did point out that at the present time, measured Cl and OCl stratospheric concentration levels are a factor of about 10 higher than current models predict and that some source of chlorine appears present which is currently not recognizable.

CCl_3COCl is usually regarded as a reactive species towards hydrolysis as are the mono and dichloroacetyl chlorides. Existing data on liquid phase hydrolysis rates for CH_3COCl and $COCl_2$[44] suggest that the latter is a factor of 6 less reactive than the acetyl chloride. If a similar reduction in sticking coefficient for $COCl_2$ occurred relative to that of CCl_3COCl,

then its atmospheric half life could fall in the 2-18 year region. Trichloroacetaldehyde, another degradation product of the chlorocarbons, due to OH radical attack, could also have a low sticking coefficient, since in this case no reaction with the water droplet, other than by solvation forces, occurs. Tempering the above estimates, it must be admitted that at the present time it is not known whether chemical reactivity or none-reactivity is associated generally with larger or smaller sticking coefficients; or if indeed there is any correlation at all.

The data presented in this section on rain out rates are preliminary in nature. Assuming the validity of the results, rain out, in the case of CCl_3COCl, would probably be a fairly efficient removal process. If the sticking coefficients for the mono, di and trichloroacetyl chlorides follow the same trend as the gas phase homogeneous hydrolysis rate constants, smaller sticking coefficients for the former two compounds, compared to CCl_3COCl would be expected. On the same basis $COCl_2$ could possibly have larger sticking coefficient than CCl_3COCl, though heterogeneous hydrolysis data would suggest the opposite effect. At the present time it is not known whether such trends apply or not. In addition to the above compounds the wash out rate for trichloroacetaldehyde should be known since this compound is produced in amounts comparable to the acetyl chlorides. This compound does not, of course, hydrolyze chemically in water, and the value of its sticking coefficient is not known.

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